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CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS OF THE YTTRIUM GROUP. I.

BY L. M. DENNIS AND BENTON DALES.

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HISTORICAL.

THE first of the rare earths was discovered by Gadolin,[1] in 1794, in a heavy black mineral which had been found at Ytterby some six years before by Arrhenius. Three years later the earth was named yttria by Ekeberg,[2] and the mineral "yttria-stone." The latter is the gadolinite of the present day mineralogists. Ekeberg[3] found yttria in a new mineral in which he had discovered tantalum and which he called yttrotantalite. The earth was further studied by Berzelius[4] and by Berlin,[5] both of whom considered it homogeneous.

Scheerer[6] observed that when yttria was heated strongly in an open vessel it took on a yellow color, which it lost on heating in the presence of reducing gases, and that it remained colorless if cooled quickly, whereas it became colored again if heated in contact with air. He thought this phenomenon due to the presence

[1] Sv. Vet. Akad. Handl., p. 137 (1794); Crell's *Ann.*, (1796) I, 313.
[2] Crell's *Ann.*, **2**, 63 (1799).
[3] Sv. Vet. Akad. Handl., p. 68 (1802); *Ann. de. Chim.*, **43**, 278.
[4] Schw. *J.*, **16**, 404.
[5] Sv. Vet. Akad. Handl., pp. 209, 212 (1835); *Ann. Chem.* (Liebig), **28**, 222.
[6] Pogg. *Ann.*, **56**, 482.

in the yttria of some other earth, perhaps new, perhaps lanthana, capable of forming easily a peroxide. His work was soon followed by the researches of Mosander,[1] who separated the old yttria into three new earths. He kept the name yttria for the most basic of these; the middle one he called terbia and the least basic one erbia. His yttria was white and gave colorless salts; terbia he thought to be white also, but it gave rose-colored salts, while erbia was orange-yellow and gave colorless salts. He used the methods of fractional precipitation of the oxalates by oxalic acid from acid solution, and of the hydroxides by dilute ammonia, in both of which his erbia was thrown out first, then terbia and lastly yttria. His results were confirmed by Berzelius[2], by Svanberg, and by Scheerer.

The earths of old yttria were reexamined in 1860 by Berlin.[3] He was the first to use the classic method of fractional decomposition of the nitrates by heat. He obtained only two of Mosander's earths, the white yttria and the one giving rose-colored salts, terbia, which he and all subsequent investigators have called erbia. Mosander's yellow erbia, the present-day terbia, he could not obtain.

Popp[4] in 1864, and Delafontaine[5] in that year and the two following ones, working at this same problem, arrived at totally different conclusions. Popp, using both of Mosander's methods, could separate neither erbia nor terbia. He thought erbia a mixture of the cerite oxides, and terbia a mixture of erbia with yttria. Delafontaine maintained that these two earths existed. Mosander's erbia he obtained by fractional precipitation with primary potassium oxalate, the small amount of yttria and terbia being removed by treatment with potassium sulphate solution. To separate the terbia and yttria remaining, he fractioned again the least-colored oxalates, then dissolved out the yttria by repeated treatment with dilute acid.

Then Bahr and Bunsen[6] in 1866, using a modification of Berlin's method of fusion of the nitrates, corroborated Berlin's results. They obtained only the true or white yttria and the rose-colored

[1] *Phil. Mag.*, **23**, 251; *Ann. Chem.* (Liebig), **48**, 219.
[2] "Lehrbuch," 2nd French Edition, **2**, 163.
[3] Scand. Naturf. 8 Möde Kjöbenhavn, p. 448 (1860).
[4] *Ann. Chem.* (Liebig), **131**, 179.
[5] *Arch. des Sci. phys. et nat.*, (2) **21**, 97; **22**, 30; **25**, 105; *Ann. Chem.* (Liebig), **134**, 99; **135**, 188.
[6] *Ann. Chem.* (Liebig), **137**, 1.

erbia of Berlin (Mosander's terbia). Cleve and Höglund[1] in 1872, using the same method, obtained the same result.

Until Mendeléeff's announcement of the periodicity of the elements,[2] yttria, ceria and the other rare earths had been generally assumed to have the formula RO. He, however, showed that their properties placed them in the third group of his arrangement, where their maximum valence would be three (oxide, R_2O_3). Lanthana he considered to be RO_2. In order to put them into this group, it was necessary to increase their accepted atomic weights by one-half. Cleve[3] in 1874, published new researches upon the salts of yttria and erbia, which tended to show the correctness of Mendeléeff's view of the triatomicity of these earths. Nilson,[4] working upon the selenites in 1875, and upon the chlorplatinum compounds in 1876, further strengthened the idea that the rare earths, lanthana included, were sesquioxides.

A great increase in activity in rare earth research occurred in 1878, when the mineral samarskite, found in large quantities in North America, became the source of the material.

Smith[5] in 1877 isolated an earth which he considered to be new, or perhaps the third earth of Mosander. He thought it new because of the insolubility of its double potassium sulphate in saturated potassium sulphate solution. Marignac[6] showed this property to be only a relative one, and he deemed Smith's mosandria to be identical with terbia. Neither could he agree to Smith's other claim that mosandria was identical with Soret's X. Delafontaine[7] considered mosandria to be terbia. Considerably later (1886), Lecoq de Boisbaudran,[8] having obtained a sample of Smith's impure mosandria, found that it contained, besides didymia and samaria, gadolinia and terbia.

Delafontaine[9] and Marignac[10] settled the question as to the existence of terbia by preparing it. Delafontaine treated his yttria earth mixture in solution with a saturated solution of sodium sulphate containing crystals of the salt, then fractioned the pre-

[1] *Bull. Soc. Chim.*, (2), **18**, 193, 289.
[2] *Ann. Chem.* (Liebig), Suppl., **8**, 133, esp. p. 184 ff.
[3] *Bull. Soc. Chim.*, (2), **21**, 344.
[4] *Ber. d. chem. Ges.*, **8**, 655; **9**, 1056, 1142.
[5] *Proc. Acad. Nat. Sci.*, Phila., **29**, 194; *Compt. rend.*, **87**, 146, 148.
[6] *Arch. des Sci. phys. et nat.*, (2), **63**, 172; *Compt. rend.*, **87**, 281.
[7] *Compt. rend.*, **87**, 600.
[8] *Loc. cit.*, **102**, 647.
[9] *Arch. des Sci. phys. et nat.*, (2), **61**, 273; *Ann. chim. phys.*, (5), **14**, 238.
[10] *Arch. des Sci. phys. et nat.*, (2), **61**, 283; *Ann. chim. phys.*, (5), **14**, 247.

cipitated portion with oxalic acid from strong nitric acid solution, and finally treated the first of these precipitates with formic acid and concentrated. Terbia crystallized out as formate. There was also a yellow earth in the portion soluble in the sodium sulphate, but it was not so deeply colored as terbia and gave besides a base of lower atomic weight. He thought it a new element. Marignac obtained terbia as well as yttria and erbia by fusion of the nitrates. By making several hundred fractions and by properly combining them he obtained finally pure yttria at one end and erbia at the other. The intermediate products possessed a yellow color. These he combined and fractioned by oxalic acid in acid solution. Erbia and didymia he found to go with terbia. Didymia he removed by the potassium sulphate treatment, but he could not free his product from erbia. Hofmann and Krüss[1] in 1893 studied terbia, and by fractionation with aniline hydrochloride succeeded in breaking it up into two probable earths with metal atomic weights of 148 to 150 and 160, calculated as R^{III}. In 1895 Lecoq de Boisbaudran[2] called attention to an absorption band in his terbia material which could not belong to any known element. He called the one which gives it Z_δ. Its band was at $\lambda 487.7$.

The new earth which Delafontaine suspected in the saturated sodium sulphate solution mentioned above, was announced by him[3] as philippia. It was characterized by a magnificent absorption band in the violet at $\lambda 450$. Soret[4] stated that philippia was identical with the earth X, which Cleve[5] denied. Delafontaine[6] maintained that philippia, Soret's X, and Cleve's holmia were identical, which Cleve again denied. Delafontaine[7] then admitted that the absorption spectrum ascribed by him to philippia belonged to Soret's X, but maintained still the individuality of the former. Roscoe,[8] in 1882, by fractional precipitation of the double potassium sulphates with potassium sulphate, and by fractionation of the first portions of these by the varying solubilities of the formates, could obtain no product whose metal had

[1] *Zischr. anorg. Chem.*, **4**, 27.
[2] *Compt. rend.*, **121**, 709.
[3] *Loc. cit.*, **87**, 559.
[4] *Loc. cit.*, **89**, 521.
[5] *Loc. cit.*, **89**, 708.
[6] *Loc. cit.*, **90**, 221.
[7] *Arch. des Sci. phys. et nat.*, (3), **3**, 246.
[8] *Ber. d. chem. Ges.*, **15**, 1274.

a constant atomic weight of 121 to 123, and he concluded that philippia was a mixture of terbia and yttria. Crookes[1] agreed with Roscoe as to the non-existence of philippia. In 1897, Delafontaine[2] gave the methods by which philippia might be prepared; they were the standard ones of fractional precipitation of the nitrate solution of the rare earths with ammonia, or with primary potassium oxalate, or fractional decomposition of the nitrates by heat. Urbain,[3] in 1900, denied the existence of philippia.

In this year of 1878, while studying the impure didymia from samarskite, Delafontaine[4] discovered a new oxide which he called decipia. Its metal had a high atomic weight ($R^{III} = 159$), and it was characterized by the absorption bands $\lambda 416$ and $\lambda 478$. Lecoq de Boisbaudran[5] found, in a spectroscopic examination of a mixture of earths rich in didymia from samarskite, some new rays. In the spark spectrum there were four rays: in the absorption spectrum, two strong bands and three faint ones. The strong bands were in the blue and had their centers at $\lambda 480$ and $\lambda 463.5$. One of the other bands had a wave-length of $\lambda 416$, which had been ascribed by Delafontaine to one of the bands of decipia. Lecoq de Boisbaudran finally separated the earth giving these bands from didymia, and he called it samaria. Then Marignac,[6] by fusion of the nitrates and fractionation of the double potassium sulphates, isolated two earths which he called Y_α and Y_β. The double potassium sulphate of Y_α was comparatively soluble in potassium sulphate solution; solutions of the earth gave no absorption spectrum, and the equivalent weight of the metal was about 120.5 (RO). Y_β, on the other hand, gave a double potassium sulphate less soluble in potassium sulphate solution; solutions of the earth gave an absorption spectrum corresponding to that of decipia or better to that of samaria, and the metal had an equivalent weight of 115.6. Y_α has since been called gadolinium.[7] Delafontaine[8] again in 1881 showed that, by treating those earth sodium double sulphates most insoluble in a saturated solution of Glauber's salt with cold

[1] *Phil. Trans. Roy. Soc.*, **174**, 910.
[2] *Chem. News*, **75**, 229.
[3] *Ann. chim. phys.*, (7), **19**, 192.
[4] *Compt. rend.*, **87**, 632.
[5] *Compt. rend.*, **88**, 322; **89**, 212.
[6] *Arch. des Sci. phys. et nat.* (3), **3**, 413.
[7] *Compt. rend.*, **102**, 902.
[8] *Loc. cit.*, **93**, 63.

water, his decipia of two years before could be decomposed into two oxides, one with a metal equivalent of about 130 (RO) giving no absorption spectrum, the other with a base of much lower equivalent (not over 117) giving the absorption spectrum ascribed to the original decipia. He expressed the opinion that this second oxide and samaria were identical, as well as Marignac's Y_β. He also thought that the earth Y_α was a mixture of decipia and terbia, but Marignac pointed out that this could not be, because the oxide of Y_α was white, whereas that of terbium was colored. The oxide of Y_α and decipia were perhaps identical.

Cleve[1] has made an exhaustive study of samaria and its compounds. He isolated it by combining the methods of fractional precipitation with potassium sulphate solution, and with dilute ammonia. The atomic weight of samarium he found to be 150.02 (R^{III}). Its spark spectrum has been described by Thalén[2] and by Lecoq de Boisbaudran[3]. The latter also studied its fluorescence spectrum. The body giving the spark spectrum he called Z_ϵ, the one giving the fluorescence Z_ζ. Demarçay[4] found that samarium could be split into at least two simpler constituents. He used three methods, Welsbach's, fractional precipitation with ammonia, and another not given. He kept the name samarium for the element giving λ 407 and λ 400, and called the other provisionally S. Krüss and Nilson,[5] in an article on the rare earths giving absorption spectra, also observed the fact that solutions containing samarium did not always give the same absorption spectrum. They obtained some solutions showing only λ 417, and the body to which this band was due they called Sm_α. Crookes[6] in 1886, following the fractionation of samarium by examination of the phosphorescence spectra, concluded that the samarium of gadolinite enclosed three components, while the samarium from samarskite contained a fourth. He[7] also observed an anomalous ray in the phosphorescence spectrum of samarium. Its wavelength was 609, and the body to which it was due he called S_α.

[1] *Compt. rend.*, **97**, 94; *Bull. Soc. Chim.*, (2), **43**, 162; *Chem News*, **53**.

[2] Sv. Vet. Akad. Handl., No. 7, p. 3 (1883); *J. de Phys.*, (2), **2**, 446; *Ber. d. chem. Ges.*, **16**, 2760.

[3] *Compt. rend.*, **114**, 575; **116**, 611, 674; **117**, 199.

[4] *Loc. cit.*, **102**, 1551.

[5] *Ber. d. chem. Ges.*, **20**, 2134.

[6] *Proc. Roy. Soc.*, **40**, 502.

[7] *Compt. rend.*, **102**, 1464.

In 1891 Bettendorff[1] obtained pure samaria by fractionation with ammonia, after the removal of ceria by fusion of the nitrates with potassium nitrate, the yttria group by treatment with potassium sulphate, and lanthana by decomposition of the nitrates by heat. He described the absorption spectrum, and denied that it had a phosphorescence one. He thought that samarium was a chemical individual. In 1893 Demarçay[2] decided that, as far as the absorption spectrum showed, there was no reason to suspect the complexity of samarium. He examined four different fractions of Lecoq de Boisbaudran's samarium material. In 1900 Demarçay[3] separated samaria from neodidymia by fractional crystallization of the magnesia double nitrates from nitric acid solution.

Crookes[4] questioned the individuality of gadolinium, stating that its phosphorescence spectrum was practically identical with that of a mixture of 61 parts of yttria and 39 of samaria. Lecoq de Boisbaudran[5] did not agree with him. Lecoq found, however, that Marignac's gadolinia contained about 10 per cent. of impurities, and he succeeded in removing all but about 0.02 or 0.03 per cent. of these. Crookes[6] described its phosphorescence spectrum, and Lecoq[7] its spark spectrum. Bettendorff[8] separated gadolinia from samaria and terbia by fractionation with ammonia. He could get no spark spectrum, nor could Thalén. In 1896 Demarçay[9] prepared gadolina by fractional crystallization of the earths rich in samaria from fuming nitric acid (sp. gr., 1.45), and gave the rays of its spark spectrum. Gadolinia was precipitated first, and samaria last. Between the two he discovered a new earth which he called Σ, characterized by its colorless salts with no absorption. The earth was colorless, which distinguished it from terbia; its spark spectrum was different from those of lanthana, ceria, gadolinia, ytterbia, terbia. It differed from gadolinia and samaria only in its spark spectrum. In 1899 Benedicks,[10] using Marignac's method partly, and partly by fusion of the ni-

[1] *Ann. Chem.* (Liebig), **263**, 164.
[2] *Compt. rend.*, **117**, 163.
[3] *Loc. cit.*, **130**, 1185.
[4] *Chem. News*, **54**, 39, 115.
[5] *Compt. rend.*, **108**, 165; **111**, 393.
[6] *Ibid.*, **102**, 646.
[7] *Loc. cit.*, **111**, 472.
[8] *Ann. Chem.* (Liebig), **270**, 376.
[9] *Compt. rend.*, **122**, 728.
[10] *Zischr. anorg. Chem.*, **22**, 393.

trates, then their fractionation from concentrated nitric acid, and lastly their precipitation by ammonia, prepared gadolinia and studied it. He could not obtain Demarçay's Σ. His gadolinia gave a spark spectrum, and the atomic weight of the metal was 156 (R^{III}). Demarçay,[1] in 1900, was unable to isolate Σ, even after 800 fractions with the magnesia double nitrates; but since then he[2] has isolated it sufficiently pure for characterization. He has named it europium.

Marignac,[3] in trying to isolate Delafontaine's philippia by partial decomposition of the nitrates by heat, discovered a new earth which he called ytterbia. It was colorless, and its metal had a high atomic weight ($R^{III} = 172.5$); further, it had no absorption spectrum. The method he used was a modification of Bahr and Bunsen's. He heated the nitrates till a portion was insoluble in hot water, whereas they heated only until the mass, which was entirely soluble in hot water, gave a crystalline precipitate of basic nitrates on cooling. In 1879 and 1880, Nilson[4], using Marignac's method, isolated more ytterbia, and studied it. He found the atomic weight of the metal ytterbium to be 173. Pure ytterbia was obtained only after 400 or 500 ignitions. While working with this material, he obtained a white oxide whose metal equivalent was lower than that of ytterbia. This caused him to suspect the presence of another oxide, the metal of which had a lower atomic weight. By following the same method of fractionation, he[5] succeeded in isolating this earth. Its base had an atomic weight of 44, and proved to be identical with Mendeléeff's ekaboron, both in its properties and its atomic weight. He called his earth scandia. Cleve[6] also prepared scandia. His atomic weight of scandium was a unit higher than Nilson's, probably because of ytterbium in the material. The spark spectrum of ytterbia has been studied by Thalén[7] and by Lecoq de Boisbaudran[8]; that of scandia by Thalén.[9]

Soret,[10] by a spectroscopic examination of Marignac's erbia and

[1] *Compt. rend.*, **130**, 1019.
[2] *Loc. cit.*, **132**, 1484.
[3] *Arch des Sci. phys. et. nat.*, (2), **64**, 97; *Compt. rend.*, **87**, 578.
[4] *Ber. d. chem. Ges.*, **12**, 550; **13**, 1430.
[5] *Ber. d. chem. Ges.*, **12**, 554; **13**, 1439.
[6] *Bull. Soc. Chim.*, (2), **31**, 486.
[7] *Chem. News*, **47**, 217; *Compt. rend.*, **91**, 326.
[8] *Compt. rend.*, **88**, 1342.
[9] *Loc. cit.*, **88**, 646; **91**, 45; *Chem. News*, **47**, 217.
[10] *Compt. rend.*, **86**, 1062.

terbia materials, found a series of absorption bands which did not belong to erbia or to any other of the known elements. He called the earth giving them X. Cleve,[1] in 1897, showed that by fractional decomposition of the nitrates by heat, erbia free from ytterbia and scandia could be separated into three earths, each characterized by an absorption spectrum which was a portion of the one ascribed to old erbia. The metals in these earths were the true erbium, with an atomic weight of about 166;[2] holmium, and thulium with an atomic weight of about 170.7.[3] Soret[4] stated that holmia and his earth X were identical, and Cleve[5] admitted this to be true. Delafontaine maintained that his philippia was identical with both of these, but Cleve could not establish this fact. Delafontaine himself afterwards admitted that his philippia had no absorption spectrum. Lecoq de Boisbaudran[6] proved, by making many hundreds of fractions with ammonia and with potassium sulphate and alcohol, that the holmia spectrum could be divided into two portions, the bands characteristic of one being λ 640.4 and λ 536.3, and of the other λ 451.5 and λ 753. Since the first two bands were the ones by which Cleve and Soret originally characterized the element holmium, he kept this name for the one giving them; the one to which the other bands were due he called dysprosium. Crookes,[7] soon after Lecoq's announcement, stated that he had isolated an earth in this group giving only the absorption band λ 451, and that therefore dysprosium was probably still a complex substance. Lecoq has expressed the same opinion. Krüss and Nilson[8] showed, by a spectroscopic examination of the absorption bands of the rare earths obtained from many different minerals, that the variations in intensities of the bands as found in these minerals, could be accounted for only upon the assumption that the bands belonged to different individuals. As a result of this, they considered what we now call erbia to be made up of two components, thulia of two, holmia of four, and dysprosia of three. Hofmann and Krüss[9] in 1893 concluded, as a result of their aniline hydro-

[1] *Loc. cit.*, **89**, 478.
[2] *Compt. rend.*, **91**, 381.
[3] *Loc cit.*, **91**, 328.
[4] *Loc. cit.*, **89**, 521.
[5] *Loc. cit.*, **89**, 708.
[6] *Loc. cit.*, **102**, 1003, 1005.
[7] *Proc. Roy. Soc.*, **40**, 502.
[8] *Ber. d. chem. Ges.*, **20**, 2134.
[9] *Ztschr. anorg. Chem.*, **3**, 407.

chloride fractionation, that holmium was a complex substance; Krüss[1] alone has thrown doubt upon the individuality of erbia. By fractionation of his material rich in erbia from alcoholic solution with an alcoholic solution of aniline, then of the middle portions of this series as earth chloride aniline hydrochloride by ammonia, he could not get an earth whose base had a constant atomic weight. The beautiful absorption spectrum of erbia was discovered by Bahr[2] in 1862. Crookes[3] mapped all of the spectra of erbia. The absorption, emission, and spark spectra of thulia have been studied by Thalén.[4]

In 1883 Crookes[5] discovered that the anhydrous sulphates of certain rare earths became phosphorescent when exposed to the electric discharge in a vacuum tube, and that this light gave characteristic spectra. He[6] had in 1881 observed that some of the earths themselves phosphoresced under the same conditions. In 1883 he discovered in these phosphorescence spectra the citron band which he decided to be due to yttria. In 1884, Lecoq de Boisbaudran[7] discovered that if the positive pole were immersed in a solution of some of the rare earths, and the negative one brought just above its surface, the light which was emitted on the passage of the spark gave an inversion spectrum which was nearly related to the phosphorescence spectrum of Crookes. Both were very delicate, and were greatly influenced by the presence of foreign oxides.

In 1886 and the year following Crookes[8] separated yttria by a large number of different fractionations into five portions, each of which had different phosphorescence spectra, but all of which showed the spark spectrum of yttria. The bodies responsible for these phosphorescence spectra he called "meta-elements," and he developed his theory of the genesis of the elements on the basis of this observation. In further support of the idea that yttria was a complex substance, he stated that Marignac's gadolinia gave him the same phosphorescence spectrum as yttria, except that the citron band was missing, and that the two green bands of samaria were present. Then a mixture of 61 parts of yttria

[1] *Loc. cit.*, **3**, 353.
[2] Sv. Vet. Akad. Handl., p. 597 (1862); *Ann. Chem.* (Liebig), **131**, 256.
[3] *Chem. News.*, **53**, 75.
[4] *Chem. News.*, **47**, 217; *Compt. rend.*, **91**, 376.
[5] *Phil. Trans. Roy. Soc.*, **174**, 891; *Chem. News*, **47**, 261; **49**, 159, 169, 181, 194, 205.
[6] *Chem. News*, **44**, 23; *Proc. Roy. Soc.*, **32**, 209.
[7] *Compt. rend.*, **100**, 1437.
[8] *J. Chem. Soc.*, **55**, 250; *Chem. News*, **54**, 115; **55**, 83, 95.

with 39 of samaria gave the same phosphorescence as gadolinia, except for the presence of the citron band. He also found that the yttria from different minerals gave phosphorescence spectra with its rays of varying intensity, showing that a partial separation had taken place in nature.

This theory and all its conclusions were opposed by Lecoq de Boisbaudran.[1] He[2] showed that pure yttria gave no phosphorescence phenomena, either by his method or by that of Crookes. According to him, the fluorescence bands were attributable to impurities, to his substances Z_α and Z_β, in fact, and these it was almost impossible to remove completely from the yttria.[3] In connection with these substances giving fluorescence bands, he[4] has studied a considerable number of fluorescences with well-defined spectral rays, having for solid solvents alumina, gallium oxide, silica, zirconia, stannic and tantalic oxides, and for active matter samaria and the oxides of Z_α and Z_β. Demarçay[5] opposed Crookes' theory of "meta-elements," and stated that the radiant matter test of Crookes was far more delicate than the reversion spectra of Lecoq de Boisbaudran.

Duboin[6] made some compounds of yttria in the dry way. The accepted atomic weight of yttrium, 89.02 with O = 16 as the standard, is the one obtained by Cleve[7] in 1882. Rowland[8] published a method for the separation of yttria from other earths of its group by means of potassium ferrocyanide. His paper was severely criticized by Crookes.[9]

In 1896 Barrière[10] announced the existence, in the yttria earths from monazite, of a new metal which was separated from the other members of the group by precipitation with sodium thiosulphate in concentrated solution. This element, lucium, had an atomic weight of 104. Crookes,[11] by examination of its spark and absorption spectra, found that it was a mixture of yttrium and didymium, erbium and terbium, but was principally yttrium. Shapleigh[12]

[1] *Bull. Soc. Chim.*, (3), **3**, 53.
[2] *Compt. rend.*, **102**, 1536.
[3] *Compt. rend.*, **103**, 113.
[4] *Loc. cit.*, **105**, 258, 301, 343, 784; **110**, 24, 67.
[5] *Rev. gen. des Sci. pures et appliqués*, **1**, 396; *Chem. News*, **62**, 85.
[6] *Compt. rend.*, **107**, 99.
[7] *Loc. cit.*, **95**, 1225.
[8] *Chem. News*, **70**, 68.
[9] *Loc. cit.*, **70**, 81.
[10] *Chem. News*, **74**, 159, 212.
Loc. cit., **74**, 259.
[12] *J. Franklin Inst.*, **144**, 68; *Chem. News*, **76**, 41.

found by a quantitative analysis of a sample of lucia that it contained 93.98 per cent. of yttria earths, 3.74 per cent. of ceria earths, 1.07 per cent. of thoria, and 1.21 per cent. of other foreign oxides.

In 1896 and 1897 Schützenberger and Boudouard[1] worked on the yttric earths of monazite sands. They found by fractional fusion of the nitrates and by fractional crystallization of the sulphates that a lower limit of fractionation was reached, giving an earth whose metal-equivalent (R_2O_3) was about 95. They thought that they had found a new earth, whose metal had an atomic weight of about 102. Drossbach,[2] working also on monazite, thought he had a new earth similar to the others (the atomic weight of its base, 100). Further, Urbain and Budischovsky,[3] fractioning the yttria earths by means of the acetyl acetonates, found a similar lower limit. Urbain,[4] working with the ethyl sulphates, succeeded in showing that this hypothetical earth could be separated into terbia ($R^{III} = 151.4$) at one end of his fractionation series, and yttria ($R^{III} = 89$) at the other. In 1900 Urbain[5] again took up the question of this earth, and concluded that it was principally yttria, mixed with some erbia and terbia. This lower limit of various fractionation series, giving a base of nearly constant atomic weight, reminds one of the "oxide of gadolinium" of Nordenskjöld.[6] This was a rare earth mixture, obtained from different minerals, which he knew to contain at least three oxides, those of yttrium, erbium, and terbium, and yet its metal had a constant atomic weight of 107.

Crookes[7] in 1898 announced the existence of an element giving a group of phosphorescence bands in the ultraviolet only. He then called it monium. Its principal rays were λ 3120 and λ 3117, and its atomic weight about 118. In 1899, he[8] renamed it victorium, and told how it was isolated. The method was a long combination of the standard ones of fusion of the yttria group nitrates, fractional precipitation of the oxalates from concentrated nitric acid solution, fusion of the nitrates again, and finally fractional precipitation with potassium sulphate.

[1] *Compt. rend.*, **122**, 697; **123**, 782; **126**, 1648.
[2] *Ber. d. chem. Ges.*, **29**, 2452.
[3] *Compt. rend.*, **124**, 618.
[4] *Compt. rend.*, **126**, 835; **127**, 107.
[5] *Ann. chim. phys.*, (7), **19**, 184.
[6] *Compt. rend.*, **103**, 795.
[7] *Chem. News*, **78**, 134.
[8] *Proc. Roy. Soc.*, **65**, 237; *Chem. Centrbl.*, (1899) II, p. 748.

In addition to all of these earths, and, of course, ceria, lanthana, didymia and thoria, a few others have been announced. Their existence was generally short. Junonium was prepared in 1811 by Thomson[1] from allanite. Donarium was announced by Bergemann[2] in 1851. He prepared it by precipitating the silica-free acid solution of the mineral thorite with ammonia. Damour,[3] Berlin,[4] and finally Bergemann himself[5] thought that donaria was identical with thoria. Bahr[6] announced the discovery of wasium, which Nicklés[7] thought was a mixture of yttrium with didymium or terbium. Delafontaine[8] thought wasium was cerium, perhaps with some didymium. Popp[9] agreed with Delafontaine. Bahr[10] considered it probable that wasium and thorium were identical, and that both Nicklés and Delafontaine were mistaken in the matter.

Smith[11] announced the existence of two new elements in samarskite, which he called columbium and rogerium. This columbium is not, of course, to be confused with the well-known one. Chroustchoff[12] detected spectroscopically the existence of a new element, russium, in certain wash residues from rocks, in many alumina preparations, and in American monazite. He[13] prepared russium in much the same manner that Barrière prepared lucium. Linnemann[14] discovered austrium in the rare earth mixtures from orthite. Lecoq de Boisbaudran[15] considered it to be gallium. Pribram[16] decided that Linnemann's product was gallium, at the same time maintaining the probability of a new element in orthite.

EXPERIMENTAL.

In 1877 J. W. Mallett published an article on sipylite, a new niobate, from Amherst County, Virginia.[17] An analysis of the

[1] Gilbert's *Ann.*, **42**, 115; **44**, 113.
[2] *J. prakt. Chem.*, **53**, 239.
[3] Pogg. *Ann.*, **85**, 555.
[4] *Loc. cit.*, p. 556 and **87**, 608.
[5] *Loc. cit.*, **88**, 558.
[6] Pogg. *Ann.*, **119**, 572; *J. prakt. Chem.*, **91**, 179.
[7] *Compt. rend.*, **57**, 740.
[8] *Ann. Chem.* (Liebig), **131**, 368.
[9] *Loc. cit.*, **131**, 364.
[10] *Loc. cit.*, **132**, 227.
[11] *Nature*, **21**, 146; *Chem. News*, **49**, 182.
[12] *Berg. u. huet. Ztg.*, **46**, 329; *Chem. Centrbl.*, p. 1277 (1887).
[13] *J. russ. phys. chem. Ges.*, **29**, 206; *Chem. Centrbl.*, **11**, 329 (1897).
[14] *Monatsh. Chem.*, **7**, 121.
[15] *Compt. rend.*, **102**, 1436.
[16] *Sitzungsber. d. k. Akad. d. Wiss., Wien*, Div. 2b, **109**, 16; *Monatsh. Chem.*, **21**, 148.
[17] *Am. J. Sci.*, **14**, 397 (1877).

mineral made under his direction by W. G. Brown indicated the substance to be essentially a niobate of erbium containing some tantalic acid, about 1 per cent. of yttrum oxide and approximately 11.5 per cent. of the earths of the cerium group.

In the following year Delafontaine[1] examined this mineral and stated that it contained erbium, philippium, and ytterbium, the last-named element having been isolated but a short time before by Marignac.

A supply of sipylite which had been procured by one of us from Virginia and Texas was used as the source of the earths in this investigation. The mineral was finely powdered and was then mixed with a large excess of primary potassium sulphate, and this mixture was fused in deep iron dishes in a crucible furnace. When decomposition was complete, the mass was cooled, powdered, and thrown into ice-water, the water being stirred until complete solution of all soluble compounds had been effected. The clear supernatant liquid was then siphoned off, nearly neutralized with ammonia, and precipitated with oxalic acid. The oxalates were then washed, dried, ignited, dissolved in sulphuric acid, and precipitated with ammonium hydroxide. This precipitate, after thorough washing by decantation, was dissolved in nitric acid and to the neutral solution there was then added a saturated solution of potassium sulphate and crystals of the same salt. The mixture was violently stirred until the supernatant liquid failed to show the absorption bands of didymium. The resulting precipitate of the earths of the cerium group was removed by filtration, and was washed with a saturated solution of potassium sulphate. The filtrate was diluted with water and was precipitated by a solution of oxalic acid. These mixed oxalates which, of course, still contained traces of the earths of the cerium group, were dried and ignited. The resulting mixture of oxides weighed about 350 grams and was of a deep orange-yellow color.

The atomic weight of the oxide mixture, assuming that all the oxides present were of the R_2O_3 type, was determined by the oxalate method of Gibbs and the sulphate method of Krüss, and was found to be in the neighborhood of $R^{III} = 108$. Assuming that the average atomic weight of the elements other than yttrum lies in the neighborhood of 165, this result shows that the mixture consists largely of yttrium oxide, approximately 75 per cent.

[1] *Compt. rend.*, **87**, 933.

The absorption spectrum when observed through a 10 cm. layer of the saturated solution of the nitrate of the mixture showed the bands tabulated below. The measurements in the table coincide with the maximum intensities of the absorption bands unless otherwise indicated.

Angle.	Wave-length λ.	Element.	Description of band.
12° 2′ 30″	6832.4	Erbium Thulium	Faint, rather broad, edges vague.
11° 45′ 10″	6670.7	Erbium	Slightly stronger than 6832.4
11° 29′ 00″ 11° 25′ 20″	6519.9 6485.7	Erbium	Moderately broad and strong with two maxima, one in center, the other at right edge.
11° 16′ 40″	6404.7	Holmium	Moderately strong, right edge sharp, maximum to right of center.
10° 11′ 50″ 10° 4′ 00″	5797.9 5725.5	Didymium	Edges of broad, very hazy band. Scarcely visible.
9° 39′ 50″	5497.7	Unknown (Crookes)	Faint.
9° 30′ 30″	5410.0	Erbium	Broad strong band, two maxima, one to left of center, the other at right edge.
9° 25′ 30″	5363.0	Holmium	
9° 11′ 10″ 9° 6′ 40″	5228.2 5185.9	Erbium	Strongest band in spectrum, two maxima, one at left edge, the other in center. Right edge indistinct.
8° 32′ 20″	4862.7	Samarium	Almost as strong as 5228.2. Extends from λ 4938.1 to λ 4825. Maximum to left of center.
8° 17′ 10″	4719.8	Samarium	Very faint.
8° 11′ 50″	4669.5	Samarium	Very faint.
7° 54′ 00″	4501.3	Dysprosium	Almost as strong as 5228.2. Extends from λ 4550.0 to λ 4449.4.
7° 43′ 40″	4403.8	Didymium (?)	Very faint.
7° 16′ 50″	4150.3	Samarium	Faint and hazy.

The measurement of the positions of the absorption bands was made with a small grating spectroscope manufactured for one of us by C. A. Steinheil Sons, of Munich. This instrument is so compact and convenient and the accuracy of the readings which can be made with it so far surpasses that attainable with a prism

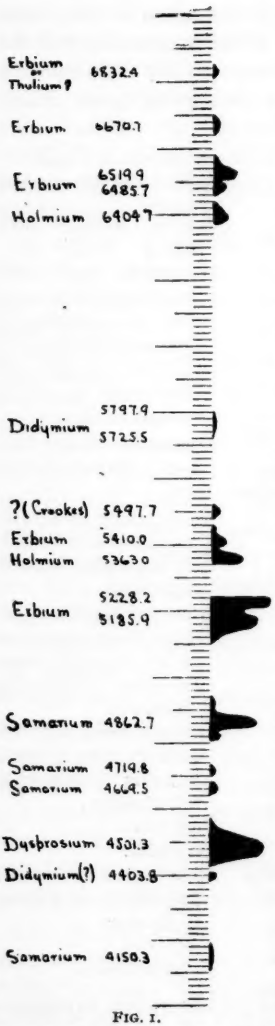


FIG. 1.

spectroscope as perhaps to justify the insertion here of a brief description of the instrument. The box of the apparatus carries the plate *EFGH* (Fig. 2) as a cover, and upon this a divided quadrant *LMN*, a vernier and a microscope. Inside the box are the grating *D*, the prism *P* and the mirror *K*. The grating is turned about the axis *a* by the vernier-arm *Q*. A is the collimator tube with slit *J*, *B* the telescope, and *C* the scale tube. The parallel rays from the collimator-objective are reflected by the prism in the direction *Pa* upon the grating *D* and from there are reflected in the direction *aO*. When the grating is so placed that the perpendicular to its plane bisects the angle *PaO*, one sees through the telescope the image of the slit reflected from the grating. The zero point of the instrument is obtained by placing the cross hairs of the eye-piece over the image of the slit. Both the quadrant and the vernier are so divided that the grating may be turned either way, the readings for the same line on either side of the zero being thus the same. The quadrant is divided into intervals of 10′; the vernier may be read to 10″. The scale tube *C* may be turned on an arm so that it may be used for spectra of the second and third orders. The wave-length of the line measured is a function of the angle through which the grating must be turned to bring the line into the position occupied by the image of the slit at the zero point. It is obtained by the formula $\lambda = \frac{K \sin \omega}{n}$, K being the constant of the instrument, and n the order

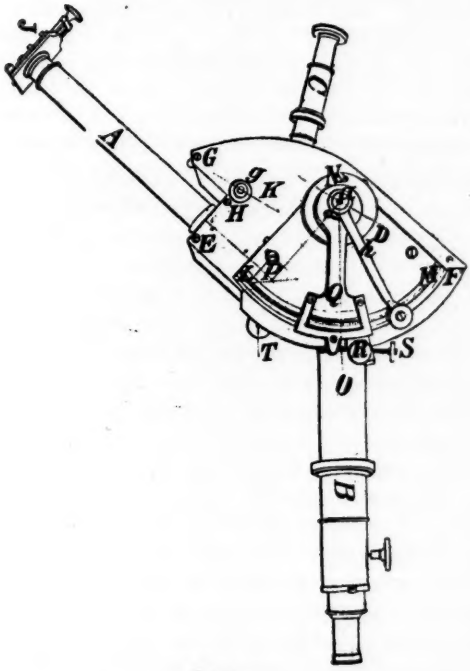


FIG. 2.

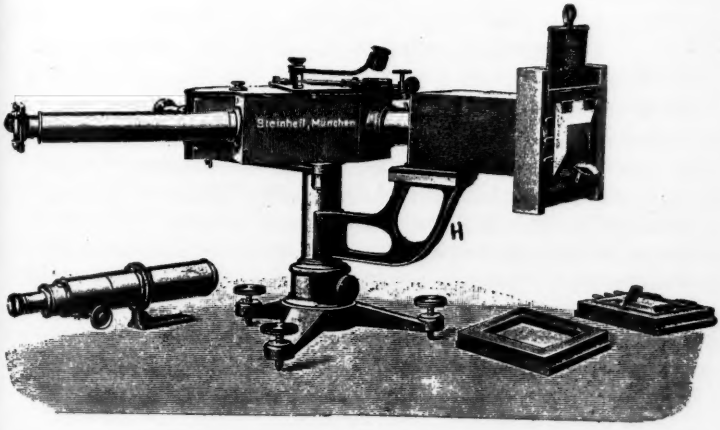


Fig. 3.

of the spectrum. Fig. 3 shows the instrument with a camera attachment substituted for the telescope tube. As the source of light a zirconia disk and a Linnemann oxyhydrogen blowpipe were used.

THE DETERMINATION OF THE ATOMIC WEIGHTS OF THE ELEMENTS.

The method described by Gibbs[1] was used when only an approximate result was desired. The procedure was as follows: A neutral or only very slightly acid solution of the earths whose atomic weight is to be determined is diluted with water, brought nearly to the boiling-point, and is then precipitated with a hot dilute solution of pure oxalic acid. The precipitate is washed by decantation and on the filter with hot water to remove the excess of oxalic acid and is then dried at a temperature of 125°. A weighed portion of the oxalate precipitate is then converted to the oxide by ignition and this oxide is weighed. Another weighed portion of the oxalate is dissolved in dilute sulphuric acid (1 : 8) and the oxalic acid is determined by titration with potassium permanganate. The atomic weight of the earths in the mixture of the rare earths is then easily calculated from the ratio of R_2O_3 : C_2O_3. This method of determining the atomic weights gives results that are sufficiently accurate to enable one to judge of the progress of a method of separation or fractionation, but which are far from being exact, and comparison of the method with the sulphate method showed that the Gibbs procedure gave results differing by as much as four units from the sulphate method of Krüss. To ascertain the effect of changes in the conditions prevailing at the time of precipitation the following experiments were made.

A solution of the earths was carefully freed from other elements by precipitating it with hydrogen sulphide, filtering off a very slight precipitate which formed, boiling the filtrate to remove the hydrogen sulphide and precipitating it with ammonia, dissolving the washed precipitate in hydrochloric acid, and after nearly neutralizing with ammonia, precipitating this solution with oxalic acid. The oxalates thus obtained were washed with very dilute hydrochloric acid (0.1 per cent.) to remove iron, then with water, and were then dried, ignited, and the resulting oxides were dissolved in hydrochloric acid. This chloride solution was divided

[1] *Am. Chem. J.*, **15**, 547.

into two parts. One was precipitated with a hot and dilute solution of oxalic acid, while the other was precipitated in the cold and in more concentrated condition with a cold concentrated solution of oxalic acid. Another portion of the same original material was purified and treated in exactly the manner described above, and was divided and precipitated in the same way. The results of the atomic weight determinations of these various portions by the oxalate method were as follows:

	Hot.	Cold.
1	111.28	108.26
2	105.06	104.70

The variations in these results show that they are greatly influenced by changes in the conditions, and that they by no means agree even when the same conditions pertain.

The other method employed for the determination of the atomic weights was that described by Krüss.[1] In this procedure the oxalate of the earth is placed in a porcelain crucible and ignited over a blast-lamp to constant weight. The crucible containing the oxide is placed on a water-bath, covered with a funnel, and the heating of the water-bath is continued until the water vapor has slowly and completely slaked the oxide. The substance is then dissolved in the crucible with dilute hydrochloric acid. A moderate excess of dilute sulphuric acid is added and the solution is concentrated as far as possible on the water-bath. The excess of sulphuric acid is removed by placing the crucible on an iron plate 5 mm. thick and heating the plate with a small Bunsen flame. This is continued until constant weight is obtained, and from the ratio of the oxide to the anhydrous sulphate, the atomic mass of the earth or earths present is calculated. Considerable difficulty was experienced in making duplicate analyses agree satisfactorily. The probable explanation of this trouble is to be found in the article by Brauner and Pavlicek,[2] in which those authors call attention to the fact that the sulphate which is finally weighed is liable to contain some acid sulphate. This acid sulphate is so stable that some of it remains undecomposed even at a temperature above 500°, while in other parts of the crucible it may have partially been broken down into a basic sulphate. They state that the error is greatest in the case of lanthanum and that it decreases as the basicity of the earth decreases. They deter-

[1] *Ztschr. anorg. Chem.*, **3**, 46.

[2] *Proc. Chem. Soc.*, London, **17**, No. 235, p. 63.

mine the amount of sulphuric acid which is present in excess over the amount necessary to form the normal sulphate by dissolving the dry sulphates in water and titrating the free sulphuric acid with a twentieth normal solution of sodium hydroxide using ethyl orange as an indicator. The normal sulphate obtained by repeated crystallization was found by them to be neutral to ethyl orange.

These statements concerning the sulphates of the earths of the cerium group hold true for those of the yttrium group, but the error is less because the basicity of the earths of this group is less. For example, two weighed portions of a sulphate which had given $R^{III} = 115.90$ and 116.42, were dissolved in water and the excess of free acid titrated as above, using methyl orange as an indicator. The corrected results for these two samples were $R^{III} = 116.19$ and 116.47. Another set which had given $R^{III} = 141.22$ and 141.53 gave after correction 141.51 and 141.73. A third set giving $R^{III} = 107.31$ and 106.75 gave after correction 107.37 and 106.92. There seems to be no regularity in the amounts of acid sulphate which are formed. The maximum error caused by its presence seems to be about 0.3 of a unit. All of the solutions which were tested showed an acid reaction, but in some cases a drop or two of the solution of sodium hydroxide was sufficient to neutralize the free acid. The results of duplicate determinations were usually brought to closer agreement by the introduction of the correction. In only one case was the opposite effect noted.

EXPERIMENTS UPON METHODS FOR SEPARATING YTTRIUM GROUP EARTHS.

The aim which the authors had in view in this work was not so much the isolation of one or another constituent of the mixture of the rare earths, but rather the study of various methods of separation to ascertain along what lines different treatments will cause the earths to separate. A complete systematic study of the different methods of separation was also not undertaken, for those procedures which give slow results and in which the successive treatments are of but slight effect upon the rare earth mixture, can not be successfully employed, because of the time which is consumed and of the incompleteness of the separation which they bring about. Therefore, in the trials of the different

methods to be described below it will be seen that the procedure was abandoned as soon as it became apparent that only slow separation was being effected.

FUSION OF THE YTTRIUM GROUP NITRATES WITH ALKALI NITRATES.

The method first tried was that of fusion of the rare earth nitrates with alkali nitrates, proposed by Debray, and which, as modified by Dennis and Magee,[1] gives such satisfactory results in separating cerium from the other members of the group. It was hoped that the decomposition points of some of the yttria group double nitrates might be found sufficiently far apart to admit of a sharp separation, but such was not the case.

The dry yttrium group nitrates were mixed with six times their weight of a molecular mixture of potassium and sodium nitrates, placed in a deep porcelain evaporator, and fused in a large double air-bath, the space between the walls of the bath being filled with infusorial earth to prevent radiation. Three fusions were made and after each the substance was extracted with hot water, yielding an insoluble and a soluble portion. Fusions were made at three temperatures, 280°, 320°, and 360°, using different mixtures each time. These temperatures were measured by means of a Le Chatelier pyrometer manufactured by Keiser and Schmidt, of Berlin. Each portion was fused for about three hours. The results were irregular and gave no indication of a sharp separation by this method, as the following atomic weights show.

Atomic weight of the initial metal mixture, 108.19.

Insoluble.	Temperature.	Soluble.
114.70	280°	108.31
127.55	320°	108.14
112.24	360°	102.43

A comparison of the absorption spectra of solutions of these portions and of the original material with a direct-vision spectroscope showed no appreciable differences.

PARTIAL PRECIPITATION WITH HYDROCHLORIC ACID GAS.

Partial precipitation of the anhydrous chlorides by hydrochloric acid gas from a cooled solution was next tried. A concentrated solution of the chlorides ($R^{III} = 107.94$) was placed in a gas wash-bottle surrounded by a freezing-mixture of ice and salt; hydro-

[1] This Journal, **16**, 653.

chloric acid gas from a Norblad generator was then passed through the liquid for about five hours. Quite a heavy white crystalline precipitate was obtained. This was thrown on to a porous plate and drained. It is very deliquescent. The concentrated solution of the crystals had a yellow color. The mother-liquor changed color from rose to orange while saturated with hydrochloric acid, due probably to the forcing back of the dissociation of the chloride by hydrochloric acid.

The mother-liquor was precipitated with ammonia and washed to remove chlorides, the precipitate dissolved in hydrochloric acid, concentrated and again treated for two hours with hydrochloric acid gas in the freezing-mixture. Another heavy white crystalline precipitate was obtained, which gave a slightly yellow solution.

The spectra of the original solution and of saturated solutions of these two precipitates were compared by means of the small comparison spectroscope manufactured by Zeiss of Jena and described by Dr. Pulfrich in the *Zeitschrift für Instrumentenkunde*, October, 1900. No changes in the relative intensities of the various bands were visible.

PARTIAL DECOMPOSITION OF THE CHROMATES.

Pattison and Clarke[1] separated cerium from lanthanum and didymium by heating the normal chromates to 230° F. for some hours. The method when tried on this material gave no separation whatever. About 3 grams of the oxides ($R^{III} = 103.75$) were dissolved in concentrated chromic acid and the solution evaporated to dryness. The dry mass was heated for six hours at a temperature of about 200° but decomposition merely on the surface was the only result, as could be told by the change in color from the red of the chromate to the green of the chromic oxide. This same substance was then pulverized and heated for six hours to 250° with practically the same result. The substance was extracted with hot water, yielding a red solution and a greenish black residue. The solution was evaporated to dryness and was then heated to 300° for eight hours, but only very slight decomposition resulted. The insoluble greenish black residue was again obtained from this portion. These two residues were treated with hot hydrochloric acid, and the green solution which was obtained was neutralized with ammonia and precipitated with

[1] *Chem. News*, **16**, 259.

oxalic acid. Only a faint trace of the rare earth oxalates were thrown down.

FRACTIONAL PRECIPITATION WITH POTASSIUM CHROMATE.

The first to use this method in the separation of the rare earths was Gerhard Krüss.[1] This has since been modified by Moissan[2] and in this form was employed by the authors on the material which gave $R^{III} = 107.94$. Krüss added a neutral solution of potassium chromate to a neutral nitrate solution of the earths, while Moissan used a sulphate solution of the earths, neutralizing the liquid with ammonium hydroxide before each fractional precipitation with potassium chromate. The authors followed Moissan's directions carefully, but used a solution of the nitrates of the rare earths instead of the sulphates. This nitrate solution, amounting to 15 liters and containing about 140 grams of the oxides was first neutralized with ammonium hydroxide and 1 liter of the solution of potassium chromate containing 97 grams to the liter was added with continual stirring. The precipitation was carried on in tall glass cylinders of about 10 liters' capacity. The flocculent precipitate was allowed to settle and the red supernatant liquid was removed by means of a siphon. The precipitate was washed with water until the wash-water gave no precipitate with ammonium hydroxide. The earths in the wash-water were recovered by precipitation with ammonium hydroxide and this precipitate was dissolved in nitric acid to a neutral solution and was added to the mother-liquor. This liquid was then again carefully neutralized with ammonium hydroxide and was then treated with the same amount of potassium chromate solution as was used for the first fraction. This procedure was repeated four times, giving in all five fractions. The mother-liquor and wash-water from the last fraction were precipitated by ammonium hydroxide yielding fraction 6. With each succeeding precipitation the dilution of the solution was increased by about 1 liter.

Precipitate 1 was so small in amount as to render its separate treatment inadvisable; it was therefore united to precipitate 2 and the two were treated as one fraction. Each precipitate was dissolved in dilute hydrochloric acid, the chromic acid was reduced by adding alcohol and heating on the water-bath, and the resulting green solution was then nearly neutralized with ammonia,

[1] *Ztschr. anorg. Chem.*, **3**, 92.
[2] *Compt. rend.*, **122**, 573.

heated to boiling, and precipitated with a boiling solution of oxalic acid. In each case the precipitated oxalates were washed with a 1 per cent. solution of hydrochloric acid and were then dried and ignited. The resulting oxide was dissolved in hydrochloric acid. For the atomic weight determinations by the Gibbs method a portion of each of these solutions was precipitated with oxalic acid and the oxalate was washed and dried.

Fraction 1 gave a pink oxalate, a deep orange oxide, and its saturated solution of a brownish-yellow color showed the same absorption bands as the original solution, but the bands were slightly stronger.

Fraction 2 was practically identical with fraction 1.

Fraction 3 gave a pink oxalate and an orange-yellow oxide somewhat lighter in tint than the oxide from fraction 2. Its saturated solution showed all of the absorption bands strongly.

Fraction 4 yielded an oxide somewhat lighter in color than that from fraction 3, and its solution showed the bands plainly but not as plainly as the preceding fractions.

Fraction 5 gave an oxalate of a pale pink color and a very light yellow oxide. The saturated solution of its oxide was much paler in color than the solutions of the preceding fractions, and while it showed all of the absorption bands they were much less distinct than in fraction 4.

Fraction 6 gave a perfectly white oxalate and the oxide showed only the faintest tinge of buff color, and its solution had a pale greenish-yellow tint. The absorption bands of this last solution were quite weak.

The atomic weights of the original material and the six fractions with fractions 1 and 2 united are as follows :

Original, 107.94.

1 and 2	3	4	5	6
133.54	126.13	114.04	97.83	94.01

Fractions 1, 2, 3, and 4 were then united and were again fractionally precipitated by the chromate method. The atomic weights of the three fractions thus obtained were 145.34, 127.38 and 103.75. The middle fraction was then split up into two parts, one showing an atomic weight of 150.03 and the other 124.53.

Fractions 5 and 6 contain yttria with about 10 per cent. of oxides having high atomic weights as terbia, erbia, and ytterbia.

These two fractions comprised nearly half the material used in the fractionation. After 7 grams of oxides with metal atomic weight of 107.07 had been extracted from them by this same process, the rest was set aside as yttria material. The two highest fractions $R^{III} = 145.34$ and 150.03 were also set aside for future use.

It is thus seen that fractionation with potassium chromate separates the earths of this group with considerable rapidity. It is especially serviceable as a means of obtaining yttria free from the other earths, this substance being separated in quite pure form at the end of a comparatively short series of fractions. The mixture of oxides in the first fractions is still a very complicated one and further application of the chromate method does not appear to affect it appreciably.

FRACTIONAL PRECIPITATION WITH PRIMARY POTASSIUM OXALATE.

The separation of the earths with this method proceeds but slowly as is shown by the atomic weights given below. The method is a modification of the one used by Delafontaine for the separation of terbia from yttria and erbia. He added the solution of primary potassium oxalate to a solution of the rare earths until a point was reached at which another drop of the reagent caused a permanent precipitate. The liquid was then allowed to stand until the oxalates crystallized out. The solid substance was then removed and crystallization was repeated after the addition of more of the oxalate.

The authors used very dilute solutions in carrying on this method of fractionation, that of the primary potassium oxalate being about one-twelfth molecular, while the solution of the rare earths was diluted until the absorption bands were just visible with distinctness. The solution of primary potassium oxalate was made by dissolving in water molecular proportions of potassium oxalate and oxalic acid.

In order to be able to judge of the effect of fractional precipitation by this method upon the absorption bands of the solution, the precipitation was carried on before the spectroscope. The solution of the rare earths was transferred to a large crystallizing dish about 20 cm. in diameter and this dish was placed directly before the slit of a Steinheil grating spectroscope. Light was furnished by a Linnemann zircon-disk lamp. The solution was

kept in constant motion by means of a stirrer run by a Porter electric motor, and the solution of the primary potassium oxalate was added drop by drop from a burette. Before beginning the fractionation it is necessary to add a concentrated solution of the oxalate until a permanent precipitate just forms.

The first effect of the precipitation was to weaken the holmium bands, while all the bands decreased in intensity, the most persistent being the erbium band in the green. About 5 grams of the oxides were obtained from fraction 1. Half of the mother-liquor from this fraction was then precipitated and 6 grams were obtained. This halving of the solution was made necessary because of the limited size of the dish, and concentration was undesirable because of the possible disturbing action of the more concentrated oxalate solution upon the earths. The mother-liquor from fraction 2 was again divided and about 5 grams of oxides were obtained in fraction 3. At the end of this third fraction all of the absorption bands had disappeared with the exception of the erbium band in the green which was just visible. The mother-liquor from the last fraction amounting to one-fourth of the original solution was completely precipitated by the addition of the concentrated solution of primary potassium oxalate. Each of the precipitates was washed, dried, ignited, and dissolved in nitric acid. The oxalates of the first three fractions were pink while that of the last one was white. The oxides of the first three fractions were orange-yellow in color while that of the last fraction had a pinkish tinge. All the solutions showed the rose-pink color of erbium salts. In determining the atomic weights, a portion of each nitric acid solution was precipitated with ammonium hydroxide and this precipitate was thoroughly washed with water to remove potassium salts. It was then dissolved in nitric acid to a barely acid solution and precipitated with oxalic acid.

Original, 112.16

1	2	3	4
118.80	116.71	111.08	102.53

The precipitates which are thrown down by these oxalate reagents are finely crystalline and are consequently easily freed from the mother-liquor. Fractionation could probably be carried on with a fair degree of rapidity and interesting results might be obtained. The separation was, however, too slow for the authors' purposes and therefore no further trials have yet been made of it.

FRACTIONAL DECOMPOSITION OF A SOLUTION OF THE MIXED NITRATES BY MEANS OF AN ELECTRIC CURRENT.

About 120 cc. of a solution of the nitrates ($R^{III} = 107.94$) were carefully neutralized with ammonium hydroxide. This solution was placed in a Classen platinum electrolysis dish and was connected with the negative terminals of two cells of a storage battery. A platinum disk about 3 cm. in diameter was used as the positive electrode. A low current of N. D.$_{100} = 0.17$ to 0.42 ampere at a potential difference between electrodes of 2.2 to 2.7 volts was passed into the solution for about twenty hours, the solution being kept neutral and at room temperature (about 21° C.). A white precipitate of the hydroxides was obtained at the cathode. A brownish deposit collected on the anode, but this was found to be lead dioxide due to a trace of lead present in the solution. The solution was poured off from the precipitate, the latter adhering to the dish sufficiently to make it possible to wash it without loss. The solution was evaporated to its original volume and was again submitted to electrolysis, with a current of N. D.$_{100} = 0.18$ to 0.20 ampere at 1.8 to 1.9 volts for seven hours at 21° C. Again there was a small amount of precipitate formed. This being non-adherent, it was removed by filtration and the wash-water and solution were again evaporated to the original volume and electrolyzed. A current of N. D.$_{100} = 0.17$ ampere failed to produce any further precipitation after six hours, so the current was raised to N. D.$_{100} = 0.33$ to 0.42 ampere with a potential difference of 2.45 to 2.55 volts and allowed to run for twenty-three hours. A further white precipitate was obtained. These two precipitates were united for the second fraction; the atomic weight of the fraction was then determined as was that of the first fraction and that of the residual solution. These three values compared with the original are as follows:

Original, 107.94.		
1	2	Residual solution.
120.22	116.61	106.20

If the decomposition voltages of the rare earths of this group were far enough apart to permit of a separation by means of electrolysis, the two fractions here should have atomic weights which differ more than do these. For if the earth or earth mixture which is thrown out of solution by a current of N.D.$_{100} = 0.17$ ampere at a potential difference between electrodes of about 2.5

volts was different from that which is precipitated by a current of about twice the density, the difference should show itself in the atomic weights. It is evident therefore that, under the conditions here prevailing, the separation of the rare earths can only slowly be effected.

FRACTIONAL PRECIPITATION WITH MAGNESIA USTA.

Muthmann and Rölig[1] separate cerium in the quadrivalent condition from lanthanum and didymium by precipitation with powdered zinc oxide, and then separate lanthanum from didymium by partially precipitating the hot concentrated solution with magnesia usta until the absorption bands of didymium have disappeared.

The effect of magnesium oxide as a precipitant was tried with a nearly saturated neutral solution of the chlorides of these yttrium earths ($R^{III} = 104.4$). Muthmann states that he stopped the precipitation when the didymium absorption bands had just disappeared. The authors found, however, that while a precipitate formed easily it would not settle sufficiently to enable the absorption bands to be observed.

The solution of the chlorides was heated to boiling, and while in vigorous ebullition, powdered magnesia was added in small quantities, with constant stirring. The precipitate which soon separated was first washed by decantation and was then washed upon a filter with hot water. The mother-liquor and the four wash-waters were evaporated nearly to saturation and the precipitation was repeated. A second repetition of this procedure gave a third fraction and the mother-liquor and wash-waters from this were then precipitated with oxalic acid for the fourth and final fraction.

Each of the precipitates was dissolved in hydrochloric acid and the solution was concentrated. These four solutions showed practically no variations in absorption bands when examined with a direct vision spectroscope. The solution from the first precipitate was treated with ammonium chloride and ammonium oxalate as Muthmann recommends, and the resulting precipitate was washed by decantation with hot water containing 0.1 per cent. hydrochloric acid and was then washed with water alone. The precipitate was free from magnesia but contained iron. The oxalates were at first non-crystalline and settled very slowly, but the

[1] *Ber. d. chem. Ges.*, **31**, 1719.

addition of the dilute acid caused them to separate in crystalline condition. It was found that, by adding oxalic acid to the neutral chloride solution of these precipitates, complete precipitation of the rare earths could be obtained and this precipitate was free from magnesia, provided ammonium chloride was present. This method of purification was therefore used with the other fractions. The oxalates from all four of the fractions were ignited and dissolved in hydrochloric acid. Since the resulting solution contained traces of iron, portions of each fraction were freed from iron by reprecipitation with oxalic acid, and the atomic weight determinations were made with this purified material. The atomic weights and absorption spectra showed that very little change had been caused in the earth mixture by fractional precipitation with magnesium oxide.

TREATMENT WITH POTASSIUM TRINITRIDE, KN_3.

The method proposed by Dennis and Kortright[1] for the separation of thorium from members of the cerium and yttrium groups, by means of potassium trinitride, was tried to see if perhaps some reaction similar to the one for thorium could be found. The results were entirely negative. Partial precipitation by potassium trinitride was found to fraction the rare earths of this group rather slowly. The precipitate in the case of thorium was thorium hydroxide. In this case it seemed rather to be a basic nitrate. It was white, very finely divided, and adhered to the beaker, and had also a tendency to go through the filter.

A dilute solution of the nitrate ($R^{III} = 112.16$) was treated with a dilute solution of potassium trinitride containing free hydronitric acid and boiled. A precipitate was obtained on boiling for two or three minutes. It was filtered, washed with hot water, dissolved in nitric acid and converted into oxalates. The atomic weight was 118.96. The nitric acid solution was pink, and the absorption bands were practically the same as in the original solution.

FRACTIONAL PRECIPITATION WITH AMMONIA.

The work of many chemists who have investigated the earths of the yttrium group has shown that these elements can unquestionably be partially separated by a long series of fractions with dilute ammonium hydroxide, but the work is so extremely tedious

[1] *Ztschr. anorg. Chem.*, **6**, 35.

and the separations are so very slow that it is questionable whether this procedure can be considered to be of material value. As an illustration of the slight effect of fractionation by this reagent one experiment will suffice.

A very dilute solution of the neutral chlorides containing about 57 grams of the oxides in 12 liters was treated with an amount of dilute ammonia sufficient to precipitate only one-tenth of the earths present. During the addition of the ammonia the solution was vigorously stirred by blowing through it a blast of air and this stirring was continued for about an hour. A precipitate formed very slowly. The hydroxides were then washed by decantation until the wash-water gave no precipitation with ammonia. The mother-liquor and wash-waters were evaporated to the original volume and precipitated again with the same amount of ammonia. The atomic weights of the earths precipitated in these two treatments were 103.9 and 104.0, while that of the original material was 96.

FRACTIONATION WITH AMMONIUM CARBONATE AND DILUTE ACETIC ACID.

Mosander[1] in 1843 mentioned that the hydroxides of the rare earths of this group are soluble in a concentrated solution of ammonium carbonate and that they could be fractioned in this way. Krüss[2] also mentioned this solubility.

This treatment alone was first tried here. The results were much better than was expected. The rare earth hydroxides were precipitated by ammonia (the latter need not be washed out). By a single treatment of these hydroxides with a quantity of a saturated solution of ammonium carbonate sufficient to dissolve one-fourth of the whole, an earth mixture was dissolved whose metal atomic weight was 121.41. The bases in the undissolved portion had an atomic weight of 107.94, while the original solution contained a metal mixture of atomic weight 108.08.

Quantities of saturated ammonium carbonate solution sufficient to dissolve other amounts of the precipitated hydroxides than one-fourth were then tried on different portions of this earth-mixture. An amount of carbonate solution sufficient to dissolve one-tenth of the hydroxides precipitated was added to one portion, while to others were added amounts of the carbonate solu-

[1] *Phil. Mag.*, **23**, 251; *Ann. Chem.* (Liebig), **48**, 219.
[2] *Ann. Chem.* (Liebig), **265**, 1.

tion sufficient to dissolve nine-tenths, one-fifth, one-third, and one-half. On the whole, however, the addition of one-fourth or perhaps one-fifth the amount of carbonate solution necessary to dissolve all the hydroxides seems to be most suitable for this method of fractionation. The total precipitation of the earths by a solution of ammonium carbonate with partial solution of the precipitate in an excess of that reagent was also tried, but this is no better than precipitation with ammonia and partial solution in ammonium carbonate. A second extraction of the hydroxides from the undissolved portion ($R^{III} = 107.94$) from the first treatment was made, and the atomic weight of the metal mixture which dissolved was 125.91. Evidently the material could be thus extracted at least twice with profit.

To the dissolved portion mentioned above ($R^{III} = 121.41$) there was then added very dilute acetic acid (1 : 30) slowly and with constant stirring, first adding concentrated acetic acid just to turbidity. This treatment had a most marked effect. The granular precipitate thrown out was of a pink color and when dissolved showed all the absorption bands very strongly, while the bands in the remaining solution were much weakened.

When the dilute acetic acid had been added as above, a point was reached at which the addition of more acid would produce no further precipitate. This is due to the fact that the rare earth hydroxides of this group are nearly as soluble in ammonium acetate as in ammonium carbonate, and a state of equilibrium is soon reached between the three, after which dilute acetic acid has no effect upon the double ammonium salts of the rare earths. It was necessary, when this point was reached, to filter, decompose the ammonium carbonate solution with hydrochloric acid, dissolve the precipitate which was formed by further addition of the acid, and then to precipitate the whole with ammonia, wash, redissolve in hydrochloric acid and reprecipitate with ammonia. The hydroxides were then dissolved in saturated ammonium carbonate solution and the precipitation by dilute acetic acid repeated.

This particular material after having been treated three times with ammonium carbonate and dilute acetic acid in the manner above described, gave a very small amount (less than 1 gram) of an earth which yielded a white oxalate and a white oxide. A determination, not in duplicate, of its metal atomic weight gave the interesting result of 170. In the dry oxide only, the green ab-

sorption band of erbium was visible by reflected light. In saturated solution this earth mixture did not show the absorption bands of holmium, thulium, nor dysprosium, but those of erbium and samarium were visible. They were, however, much weaker than in the original solution. The spark spectrum of this solution was also examined, and the following lines of ytterbium as given by Thalén[1] were found:

Angle.	Wave-length.	Thalén's measurements.
10° 57′ 00″	6220.9	6221.0 (1)
9° 46′ 00″	5555.6	5555.5 (1)
9° 37′ 30″	5475.7	5476.0 (1)
9° 24′ 30″	5353.5	5352.0 (1)
9° 22′ 30″	5334.8	5334.0 (1)
9° 18′ 50″	5300.3	5300.0 (4)
8° 24′ 10″	4785.7	4785.5 (2)
8° 17′ 40″	4724.5	4725.0 (2)

The spark spectra of erbium and samarium were very weak. None of the characteristic gadolinium lines were found. The mixture was, therefore, ytterbium and erbium with some samarium, but no holmium, thulium, or dysprosium, no yttrium, gadolinium, or terbium.

To show further the effectiveness of this method of fractionation, it was tried on nearly all of the material in hand. The material was divided into two parts, in one of which the bases had an atomic weight of 117.37 and in the other of 107.15. Each of these portions was carefully purified by treating the boiling, slightly acid chloride solution with hydrogen sulphide, filtering, boiling to expel hydrogen sulphide, then precipitating with ammonia and washing, dissolving the precipitate in dilute hydrochloric acid, neutralizing and precipitating with oxalic acid solution, stirring the while by blowing air through the solution. The oxalate precipitate was washed with 0.1 per cent. hydrochloric acid to remove iron, then with water, dried, ignited, and dissolved in hydrochloric acid. The atomic weights given above were obtained from the material thus purified by precipitating this chloride solution again with oxalic acid, both solutions being boiling hot.

The details of the treatment for the solution ($R^{III} = 117.37$) were as follows: The chloride solution was divided and placed in three tall cylinders, diluted and precipitated with ammonia.

[1] *J. de Phys.*, (2), 2, 37.

The hydroxides were washed, then dissolved completely in saturated ammonium carbonate solution, and concentrated acetic acid added just to turbidity. Then to each of the three cylinders was added 1000 cc. of dilute acetic acid (1 part acid diluted to 30 with water) in small quantities at a time and with constant stirring by a current of air. The flocculent precipitate soon became granular and could easily be separated from the mother-liquor by decantation. The last of the mother-liquor was removed from this fraction 1 by suction. Dilution with water caused the earths to precipitate from the ammonium carbonate solution; therefore the mother-liquor could not be washed out. The mother-liquors were treated with concentrated hydrochloric acid till the ammonium carbonate was destroyed and the resulting hydroxides dissolved, then precipitated with ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia; then these hydroxides were treated again with saturated ammonium carbonate solution. This time the carbonate solution was placed in two cylinders, the excess of ammonium carbonate neutralized by concentrated acetic acid and 700 cc. of dilute acetic acid added to each one slowly and with constant stirring. The precipitate was fraction 2.

The mother-liquors here were removed and decomposed exactly as before, and the ammonium carbonate solution of the hydroxides neutralized with concentrated acetic acid and treated in one cylinder with about 600 cc. of dilute acetic acid (fraction 3). The mother-liquor from this fraction still showing a trace of the erbium band in the green after its conversion by the usual decomposition into chloride solution and concentration, it was diluted, precipitated with ammonia, dissolved in saturated ammonium carbonate solution as before and precipitated this time after neutralization by about 30 cc. of dilute acetic acid. The precipitate (fraction 4) was, of course, slight. The mother-liquor from it was dissolved in hydrochloric acid, nearly neutralized with ammonia and precipitated with oxalic acid to remove most of the iron. The oxalates were washed, dried, ignited, and dissolved in hydrochloric acid. This solution concentrated to saturation gave three absorption bands, the red and the green of erbium, and the samarium band between the blue and the green, none of them strongly. The atomic weights of the bases for the series were:

Original, 117.37.

1	2	3	4	Residual mother-liquor.
115.25	116.33	141.62	159.78	165.48

The other material (R = 107.15) treated in the same manner yielded the following series of atomic weights:

1	2	3	4	Residual mother-liquor.
105.33	102.4	110.6	119.45	146.53

It is worthy of note here that the metal atomic weights of the first two of the fractions in each of these series are quite close together, while those of the other fractions show a marked divergence from one another. In the second series the curve of atomic weights even goes through a minimum. There are two reasons for the apparent non-fractionation in these first two fractions. One is that the larger portion of the material used was precipitated in these first two fractions. The other and more important one is that the erbium ($R^{III} = 166$), terbium ($R^{III} = 159$), and yttrium ($R^{III} = 89$) have so distributed themselves in the first and second fractions, more terbium in the first, more erbium in the second, that the atomic weights of the metal mixtures are about the same.

The changes in color of the ignited oxides from these series were very marked. In the first series the original earth was a deep orange-yellow color. No. 1 gave a more deeply colored earth, No. 2 was chamois-colored, No. 3 pink, No. 4 white with a pinkish cast, and the earth from the mother-liquor almost white. In the second series the earth from the original solution had a deeper orange-yellow color than that from the other original solution. No. 1 was more deeply colored yet than this original solution, No. 2 lighter, No. 3 chamois-colored, No. 4 the same, and that from the mother-liquor white with a pinkish cast.

This color change evidences a marked change in the terbium content of the various fractions. Terbium concentrates very markedly in the first fractions. It is true that much the larger portion of the earths was thrown out in the first fraction in these two series, but by a short systematic fractionation, erbium material can unquestionably be obtained terbium-free.

This method seems then to offer a method for the comparatively rapid concentration of terbium with yttrium at one end of the series, and of erbium and ytterbium at the other. Holmium, thulium, and dysprosium concentrate in the middle fractions.

The results thus far obtained in this investigation may be briefly summarized as follows :

The Gibbs method of determining the equivalent weight does not give exact results even when the conditions prevailing in different series of determinations are identical.

There is a slight error in the sulphate method of determining the equivalent weights, due to the formation of some acid sulphate.

Of the many methods of partial precipitation which were investigated the following seem to be the most rapid : primary potassium oxalate, potassium trinitride, partial decomposition by fusion of the nitrates with alkali nitrates, and electrolysis of neutral solutions. Magnesia usta causes fractionation of this material, but the progress of the separation can not be easily controlled with the spectroscope as was done by Muthmann in his work on didymium.

One of the best methods for the separation of yttria from the other members of this group is that of fractional precipitation of a neutral solution by potassium chromate. Quite pure yttria may be obtained in this manner at the end of a comparatively short series of fractions.

Unusually rapid separation of the earths of this group is effected by ammonium carbonate and acetic acid. Fractional solution of the hydroxides by means of a saturated ammonium carbonate solution causes quite rapid separation, and if this ammonium carbonate solution be fractionally precipitated by addition of acetic acid, the results are most striking. Ytterbium is the last of the earths to be precipitated by this treatment. Erbium and terbium concentrate in the first fraction.

CORNELL UNIVERSITY,
January, 1902.

ELECTROLYTIC DEPOSITION OF LEAD FROM A PHOSPHORIC ACID SOLUTION.

BY A. F. LINN.

Received January 20, 1902.

LEAD has been successfully deposited as metal, by the electric current, from a solution of the double oxalate, the acetate, the oxide in sodium hydroxide, and also the phosphate dissolved in the latter reagent.[1] From each of these solutions the separa-

[1] Smith's "Electrochemical Analysis," p. 62.

tion of metal is complete and satisfactory, but the results are almost invariably too high, owing to the tendency of the moist deposit to undergo partial oxidation.

Smith therefore recommends the employment of a nitric acid solution containing from 10 to 20 per cent. of free acid, from which the lead separates as dioxide upon the anode. Some interesting results have been obtained by Smith[1] in the electrolysis of metallic phosphates in acid solution, but as far as the writer is aware, no experiments are recorded showing the deportment of lead toward the current in the presence of an excess of phosphoric acid. Preliminary trials showed that the metal could be deposited from a solution of this kind completely, and in such a form as to warrant a more extended study. The phosphoric acid used had a specific gravity of 1.71. In an excess of acid of this strength lead phosphate, precipitated either by disodium hydrogen phosphate or phosphoric acid, is readily soluble. With such a solution the following experiments were made.

The method of working was to take a definite volume of lead nitrate solution, precipitate the phosphate by disodium hydrogen phosphate or phosphoric acid, dissolve this in an excess of the phosphoric acid, and then electrolyze by a current of known strength. The deposited metal was washed with freshly boiled distilled water, absolute alcohol and ether, and finally dried in an air-bath at 100°–110° C. The deposition of metal took place at ordinary temperatures.

From a solution, prepared by precipitating lead phosphate by phosphoric acid, and then dissolving this in an excess of the precipitant, the lead separates in a partly crystalline and partly spongy condition, but sufficiently adherent to allow of thorough washing. If the amount of lead in the solution is too great, or the current too strong, the deposit is always very spongy and some of it is apt to be carried away in the washings.

On the other hand, from a solution made by adding more than enough disodium hydrogen phosphate for complete precipitation of lead phosphate, and then dissolving this in an excess of phosphoric acid, the lead deposit forms on the platinum dish a smooth, uniform, gray coating similar to that produced from an alkaline solution of lead. In a few experiments some brown discolorations were noticed on the dried deposit. These were taken to indicate

[1] *Am. Chem. J.*, **12**, 329, and **13**, 206.

oxidation. Throughout the course of this work the tendency of the deposit to oxidize in the drying process did not give much difficulty, if after a thorough washing with ether the latter is evaporated by the heat of the hand before the crucible or dish is placed in the air-bath.

The greatest difficulty encountered was the readiness with which the moist deposit dissolved in the wash-water after the current was interrupted. After a number of trials it was found best to allow the current to act during the washing with water, then to *very rapidly* wash with a small amount of absolute alcohol, and finally with ether as stated above.

When a strong current was used, or even in the case of a weaker current allowed to act for a longer period than is required for the complete deposition of the lead, the deposit gave a test for phosphorus, and the platinum vessel in a number of experiments was found to be stained a light brown color after the solution of the deposited lead in warm moderately concentrated nitric acid. The brown stain seems to be insoluble in any single acid hot or cold. Preliminary tests show that it contains both lead and phosphorus. This substance, probably a phosphide of lead, is under examination at the present time.

Experiments 1–7 show that with a fairly strong current the lead separates in the spongy condition and is especially difficult to wash, without loss due to the solvent action of the wash-water. In No. 2 the lead deposit, after the first weighing, was allowed to stand in contact with 20 cc. distilled water for three minutes, then washed with alcohol and ether, dried and weighed again. The loss in weight was 2 mg., and the washings, which contained no solid particles mechanically removed, showed a strong test for lead with hydrogen sulphide.

In 9–12 the current acted for a much longer time than was required for complete deposition. In each case, the deposited lead when dissolved in moderately concentrated nitric acid gave a test for phosphorus, and the platinum dish showed the brown stains already mentioned.

Experiments 13–18 show that under the conditions given, lead can be deposited satisfactorily from a phosphoric acid solution. The results obtained would indicate that in a solution containing not more than one-tenth gram of lead, and to which about 10 cc. of sodium phosphate, and 12–14 cc. of phosphoric acid (sp. gr.

No.	Lead taken. Gram.	Lead found. Gram.	Diff. Per cent.	$N.D._{100}$. Ampere.	Voltage.	Hrs.	Dilution. cc.	H_3PO_4. cc.	Na_2HPO_4. cc.	Remarks.
1	0.0937	0.0912	−2.6	0.018	3.5	2	130	..	..	Very spongy. Not all deposited by current.
2	0.0937	0.0917	−2.1	0.018	3.5	4	130	10	10	Spongy. Precipitation complete. Pb found in washings by H_2S.
3	0.0717	0.0700	−1.8	0.018	3.5	7	130	10	10	Spongy. Precipitation complete. Pb found in washings by H_2S.
4	0.0717	0.0730	+1.8	0.018	3.5	12	130	10	10	Spongy. Brown spots after drying.
5	0.0143	0.0150	+4.8	0.018	3.5	3	130	10	.	Spongy. Brown spots after drying.
6	0.0717	0.0711	−8.3	0.018	3.5	3	130	10	..	Deposition complete. Pb found in washings by H_2S.
7	0.1151	0.1148	−0.26	0.018	3.5	4	130	10	..	Spongy but adherent. No test for Pb in washings.
8	0.0344	0.0369	+7.2	0.002	3	20	130	14	..	P in deposit.
9	0.0344	0.0340	−1.1	0.011	3	5	130	14	..	Spongy. Pb found in washings.
10	0.0344	0.0356	+3.4	0.002	3	17	130	10	..	P in deposit.
11	0.0562	0.0575	+2.3	0.002	3	17	130	14	..	P in deposit.
12	0.0206	0.0205	−0.48	0.002	3	4.5	130	10	8	Deposition complete.
13	0.0344	0.0342	−0.58	0.003	3	5	130	7	5	Deposition complete.
14	0.0562	0.0560	−0.35	0.002	3	7	130	12	10	Deposition complete.
15	0.0562	0.0561	−0.17	0.002	3	6	130	12	8	Deposition complete. Washed with hydrant water.[1]
16	0.0937	0.0934	−0.32	0.003	3	8	130	12	8	Deposition complete.
17	0.0937	0.0932	−0.53	0.003	3	8	130	12	10	Deposition complete. Washed with hydrant water.
18	0.0562	0.0559	−0.53	0.002	3	10	130	8	6	Deposition complete.

[1] Contains about 28 grains solids per gallon, consisting mainly of the carbonates of calcium and magnesium.

1.71), have been added, the metal can be quantitatively separated by a current having $N.D._{100} = 0.003$ ampere, and voltage 3. The deposition is complete in twelve to fourteen hours.

SEPARATION OF LEAD FROM MANGANESE.

Phosphate of manganese is readily soluble in an excess of phosphoric acid. With such a solution several trials showed that even strong currents produced no effect other than to develop a pink coloration, suggesting the color of weak permanganate.[1] The current was allowed to act at ordinary temperatures for seventeen hours.

When lead and manganese were in the same solution and electrolyzed with

$N.D._{100} = 0.011$ ampere,
Voltage = 3,
Dilution = 130 cc.,
Phosphoric acid = 14 cc.

manganese dioxide was thrown out on the anode, while the lead deposit gave tests for both lead and manganese.

Further work is now being done to determine whether lead can be separated from manganese in a phosphoric acid solution.

WITTENBERG COLLEGE, SPRINGFIELD, O.,
December 26, 1901.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(THIRD PAPER.)

BY HENRY L. WHEELER AND HENRY F. MERRIAM.

Received February 14, 1902.

IN our first paper[2] we described the results of an examination of rhodanides formed from certain alkylmonohalides and potassium thiocyanate, and showed that it is a simple matter to distinguish normal from isothiocyanates by their behavior with thiol acids.

In the case of monothiocyanates, two reactions were observed. Either a direct addition was obtained with the formation of benzoyldithiourethanes, or along with other products, an ester of thiobenzoic acid resulted. The latter reaction was observed only in the case of certain secondary and tertiary thiocyanates:

[1] Smith: *Am. Chem. J.*, **12**, No. 5.
[2] This Journal, **23**, 283 (1901).

$$C_6H_5CO.SH + NCS.CH_2R = C_6H_5CONHCS.SCH_2R$$

and

$$C_6H_5CO.SH + NCS.CRR'R'' = C_6H_5CO.SCRR'R'' + HNCS.$$

On the other hand, isothiocyanates reacted smoothly to form benzamides and carbon disulphide:

$$C_6H_5CO.SH + SCN—R = C_6H_5CONHR + CS_2.$$

The work has now been extended to dirhodanides, and incidentally it has been found that not all dihalides yield dirhodanides.

The dirhodanides which have been obtained from dihalides and potassium thiocyanate have, without exception, proved to be derivatives of normal thiocyanic acid.

We have found that the action of thiobenzoic acid, in the case of 1,1-dithiocyanates, as represented by methylene thiocyanate, and of 1,2-dithiocyan derivatives, ethylene and phenylethylene (styrolrhodanide), is by no means as smooth or simple as that in the cases previously described. In fact, even when the action was moderated by heating in the presence of benzene, thick oils or varnishes were invariably formed in addition to material that could be crystallized.

From methylene thiocyanate and thiobenzoic acid, three crystalline products were directly obtained. These, we have concluded, are methylene dithiourethane (I), benzoyldithiocarbamicmethylenethiolbenzoate (II), and the methylene derivative of benzoyldithiocarbamic acid (III):

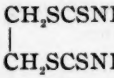
$CH_2(SCSNH_2)_2$. I.

$C_6H_5CO.SCH_2S.CSNHCOC_6H_5$ II.

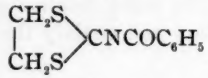
$CH_2(SCSNHCOC_6H_5)_2$. III.

During the reaction, hydrogen cyanide and carbon disulphide were formed, the latter being due to a secondary reaction of thiocyanic acid, HNCS.

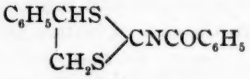
In the case of ethylene thiocyanate, we isolated two products. These were ethylene dithiocarbamate (IV), and the benzoyl-derivative of imidomethyleneethylene disulphide (V), while phenylethylene gave the corresponding imidomethylenephenylethylene disulphide (VI):



IV.



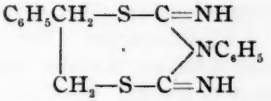
V.



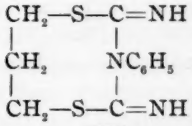
VI.

As an example of a 1,3-dithiocyanate, trimethylene rhodanide was examined. This reacted in the normal manner for a primary thiocyanate, and a bisdithiourethane was smoothly formed.

A property which appears to be unique for normal thiocyanates was observed in the case of trimethylene and phenylethylene thiocyanates. These compounds combine directly with one molecular proportion of aniline, probably to form seven- and eight-membered rings, the behavior being somewhat similar to that when pseudothiohydantoïns are formed by the action of bases on ethylphenylthiocyanacetate, etc. The compounds may be viewed as cyclopseudophenyldithiobiurets. If tautomeric forms are excluded, two isomers are possible in the case of trimethylene thiocyanate, while from phenylethylene there are three. In the latter case, the end nitrogen atoms have different positions in respect to the phenyl group (VII). Since the trimethylene compound was not obtained from phenyldithiobiuret, $C_6H_5NHCSNHCSNH_2$, trimethylene bromide, and alkali or ammonia, it appears that the following formulas best represent the structure of these compounds:



VII.



VIII.

There seems to be no mention in the literature of dithiocyanates derived from 2,3-dihalides, and it is a noteworthy fact that such dihalides of this type, as we have examined, react with alcoholic solutions of potassium thiocyanate in a peculiar manner.

In each case, with the exception of isoeugenolmethyletherdibromide, the yellow, amorphous material or mixture called pseudocyanogen sulphide[1] was formed in more or less amount. In these cases, the halides act like free bromine on potassium thiocyanate.

In addition to pseudocyanogen sulphide, 2,3-dibrombutane, $CH_3CHBr—CHBr—CH_3$, gave a yellow oil. This was found to decompose on distilling under reduced pressure. The oil was, therefore, simply washed and then dried in a vacuum. A nitrogen determination gave 12.2 per cent., while the calculated for butylene dithiocyanate is 16.2 per cent. nitrogen. These figures

[1] Goldberg: *J. prakt. Chem.*, **64**, 166 (1901).

are given here merely to show that, in all probability, a dithiocyanate is formed in this case. Pinacone dibromide $(CH_3)_2CBr\ CBr(CH_3)_2$ and allylbenzene dibromide, $C_6H_5CHBrCHBrCH_3$, behaved in a similar manner.

2,4-Dinitrostilbene dibromide $C_6H_3(NO_2)_2CHBrCHBrC_6H_5$, dibrommethylhydrocinnamate, $C_6H_5CHBr—CHBrCO_2CH_3$, and the dibromide from the nitrile of phenylcinnamic acid, $C_6H_5CHBr—CBr(CN)C_6H_5$, when warmed with alcoholic potassium thiocyanate gave abundant precipitates of pseudocyanogen sulphide. In these cases, the bromine was simply removed and the compounds were converted into the corresponding unsaturated products from which the bromides were prepared.

The property of forming pseudocyanogen sulphide is not confined to 2,3-dihalides, since it has been found that certain tertiary halides behave in like manner.

We have found that 1,2-dibromisobutane, $(CH_3)_2CBrCH_2Br$, gives pseudocyanogen sulphide. Monobrombenzylcyanide and bromcyanethyl acetate react in the same manner. Eugenol tetrabromide, $C_6H(OH.OCH_3Br_2)CH_2CHBrCH_2Br$, gave no pseudocyanogen sulphide, nor did isoeugenol methyl ether dibromide, $C_6H_3(OCH_3)_2CHBr—CHBrCH_3$, a 2,3-dibromide. The exceptional behavior of the latter compound shows that the formation of pseudocyanogen sulphide is not general in the case of 2,3-dibromides. That this dibromide has the structure assigned to it, and that isoeugenol methyl ether does not add bromine in the 1,4 position, *i. e.*, part in the nucleus and part in the side-chain, has been proved by us by oxidation with potassium permanganate, whereupon veratric acid and dimethoxyphenylglyoxylic acid[1] were obtained.

EXPERIMENTAL PART.

Methylene, Thiocyanate and Thiobenzoic Acid.—Nineteen grams of the thiocyanate and 35 grams of the acid were dissolved in about two volumes of benzene and the mixture was heated on the steam-bath. After five or six hours it was found that yellow crystals had separated. Ten cc. of the benzene was then distilled off and found to contain hydrogen cyanide and carbon disulphide. The insoluble material, after washing with benzene, was crystallized from glacial acetic acid, whereupon, on slowly cooling, it separated in the form of small, slender, pointed, pale

[1] Ciamician and Silber: *Ber. d. chem. Ges.*, **23**, 1164 (1890).

yellow prisms. It melted, not sharply and with effervescence, at 166°. The yield was about 4 grams, and on analysis the following results were obtained:

	Calculated for $C_3H_6N_2S_4$.	Found. I.	Found. II.
Nitrogen	14.1	14.2	13.9
Sulphur	64.6	65.5	...

The nitrogen determinations agree with the calculated for *methylene dithiocarbamate*, $H_2NCS.SCH_2SCSNH_2$, and this structure is confirmed by the fact that the compound dissolves in alkali and undergoes decomposition into methylene mercaptan and thiocyanic acid.

The benzene filtrate from the above was evaporated in a vacuum, and the thick oil thus obtained was stirred with ether containing a little alcohol. The solid material, thus produced, was crystallized from alcohol and benzene, whereupon yellow elongated plates melting at 138°–139° were obtained. The yield was about 4 to 5 grams, and analysis gave the following results:

	Calculated for $C_{16}H_{13}O_2NS_3$.	Found. I.	Found. II.
Nitrogen	4.03	4.33	4.56
Sulphur	27.66	28.46	27.68

Since the material is soluble in alkali with decomposition and has a yellow color, the assumption that it contains a dithiourethane grouping seems justified. In view of the above analyses, this would then permit of the following structural formula:

$$C_6H_5CONHCS.SCH_2SCOC_6H_5.$$

The substance is, therefore, a *methylene ester of thiobenzoic and benzoyldithiocarbamic acids.*

The ether solution from the above was shaken with alkali and precipitated with carbon dioxide. The resulting oily solid was crystallized from benzene and ligroïn, whereupon bright yellow crystals melting at 130°–131° were obtained. The yield, owing to decomposition by alkali, was less than a gram and a nitrogen determination gave:

	Calculated for $C_{17}H_{14}O_2N_2S_4$.	Found.
Nitrogen	6.89	7.14

This corresponds to the calculated for, the methylene ester of benzoyldithiocarbamic acid, $(C_6H_5CONHCS.S)_2CH_2$.

Methylene Thiolbenzoate, $(C_6H_5COS)_2CH_2$.—The possibility

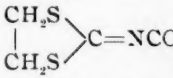
suggested itself that the solubility of the above compounds in alkali might be due to the presence of two negative groups attached to methylene and not to a dithiourethane group. In order to decide this point, we have prepared the methylene ester of thiolbenzoic acid by treating potassium thiolbenzoate with methylene iodide. The mixture in alcoholic solution reacted at once, and the product formed long, snow-white needles melting at 120°. It is insoluble in, and remains unaffected by dilute alkali. A sulphur determination gave:

	$C_{15}H_{12}O_2S_2$.	Found.
Sulphur	22.22	22.31

Ethylene Thiocyanate and Thiobenzoic Acid.—Thirty grams of ethylene thiocyanate were heated on the steam-bath, for six to eight hours with 56 grams of thiobenzoic acid, diluted with 125 cc. of benzene, whereupon it was found that a crystalline precipitate had separated. About 10 cc. of the benzene were then distilled off, and this gave the reactions for carbon disulphide and hydrogen cyanide. The insoluble material was crystallized from glacial acetic acid and, on slowly cooling, it came down in aggregations of flattened prisms, of a very pale cream color. Thirteen grams of this material were obtained melting, not sharply, at 188°–189°. The analytical results were as follows:

	Calculated for $C_4H_8N_2S_4$.	Found.
Carbon	22.6	22.2
Hydrogen	3.8	3.6
Nitrogen	13.2	13.7

Since the material, on treating with alkali, is smoothly decomposed into ethylene mercaptan and thiocyanic acid it follows that the substance is *ethylene dithiocarbamate*, $H_2NCS.SCH_2CH_2S.CS\text{-}NH_2$. The second product was obtained by partly evaporating the benzene from the above filtrate, whereupon beautiful, colorless prismatic tables separated. These were crystallized from alcohol and benzene, and melted then at 80°–81°. The yield was 20 grams and a nitrogen determination agreed with the calculated for *benzoylimidomethyleneethylene disulphide*,



	Calculated for $C_{10}H_9ONS_2$.	Found.
Nitrogen	6.27	6.24

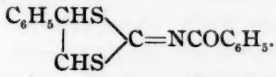
The structure of this compound was proved by preparing it from the so-called rhodanethylsulfin hydrochloride[1] and benzoyl chloride by means of the Schotten-Baumann reaction. The two products were identical in every respect. This excludes the possibility that the compound prepared by Miolati, melting at 141°–143°, is, as he supposed, benzoylimidomethyleneethylene disulphide.

When the material was treated with aqueous alkali it remained insoluble and apparently unaffected. With strong alcoholic potash it readily dissolved and was decomposed into ethylene mercaptan, (ethylene tetrasulphide), thiocyanic acid, benzoic acid, and probably some ethylbenzoate.

Chlorethylene Thiocyanate and Thiobenzoic Acid.—When these substances were heated together on the steam-bath, in benzene solution, a white solid separated. This was crystallized from alcohol and ether. Colorless, thin, square plates were thus obtained which blackened about 200°, and melted with decomposition about 212°. This material is soluble in water and the solution gives a crystalline compound with stannous chloride. Its properties and the following nitrogen determination show that the substance is *imidomethyleneethylene disulphide hydrochloride*.

	Calculated for $C_3H_6NClS_2$.	Found.
Nitrogen	9.00	9.02

Styrol thiocyanate and thiobenzoic acid, in molecular quantities, were heated in benzene for a number of hours. The presence of carbon disulphide was then detected and, on evaporating some of the benzene, solid material was obtained. This crystallized from alcohol in thin plates and melted at 135°. The following analysis shows that this compound is *benzoylimidomethylenephenylethylene disulphide*,



	Calculated for $C_{16}H_{13}ONS_2$.	Found.
Carbon	64.21	64.62
Hydrogen	4.34	4.85
Sulphur	21.40	22.27
Nitrogen	4.68	4.65

When this was warmed with alcoholic potash it decomposed,

[1] Miolati: *Ann. Chem.* (Liebig), **262**, 61.

giving benzoic and thiocyanic acids. A colorless transparent varnish was also obtained but not further examined.

Trimethylene Thiocyanate and Thiobenzoic Acid.—Thirty grams of thiobenzoic acid and 17 grams of trimethylene thiocyanate were diluted with 50 cc. of benzene and heated on the steam-bath for ten hours. Ten cc. of the benzene were then distilled off, and the fact that carbon disulphide and hydrogen cyanide were present was established. On allowing the reaction product to cool, a yellow crystalline mass was obtained. This was crystallized from benzene and ligroïn, whereupon it came down in long slender yellow prisms melting at 154°–155°. The yield was about 30 grams. It was soluble in aqueous alkali and was precipitated with more or less decomposition by carbon dioxide. A nitrogen determination gave:

	Calculated for $C_{19}H_{18}O_2N_2S_4$.	Found.
Nitrogen	6.45	6.39

This is, therefore, *trimethylenebenzoyldithiocarbamate*, C_6H_5CO $NHCS.SCH_2CH_2CH_2S.CSNHCOC_6H_5$.

Trimethylene Thiocyanate and Aniline.—Five grams of trimethylene thiocyanate were heated with three grams of aniline, on the steam-bath, for twenty-four hours. The product was diluted slightly with alcohol, and then ether was added until no further precipitate was formed. On crystallizing from alcohol and ether, colorless transparent tables or prisms were obtained. These sintered at about 168° and melted at 173°. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}N_3S_2$.	Found.
Nitrogen	16.73	16.72

This result agrees with the calculated for, a *pseudomethylene-phenyldithiobiuret.* Attempts to prepare this from phenyldithiobiuret, $C_6H_5NHCSNHCSNH_2$, and alkali or sodium ethylate and trimethylene bromide gave only a yellow, extremely sticky varnish from which nothing was obtained in crystalline form. When aqueous ammonia was employed instead of alkali, a method used with success by Tursini[1] for the preparation of an ethyl derivative, the result was similar, except that in one case a very small amount of well-developed crystals were obtained, melting sharply at 109°.

Styrol Thiocyanate and Aniline, when heated on the water-bath

[1] *Ber. d. chem. Ges.*, **17**, 585 (1884).

in molecular proportions, gave a gummy mass. This was dissolved in a little alcohol, and ether added until no more solid was precipitated. On crystallizing from a mixture of alcohol and ether, colorless plates, melting at 205°, were obtained. The analysis showed that this material is a *pseudophenylethylenephenyldithiobiuret*:

	Calculated for $C_{10}H_{16}N_8S_2$.	Found.
Nitrogen	13.41	13.32
Sulphur	20.45	21.07

Metaxylylene Thiocyanate, $C_6H_4(CH_2SCN)_2$, from metaxylylene bromide and potassium thiocyanate, forms colorless prisms, when crystallized from alcohol, melting at 160°–161°. A nitrogen determination gave:

	Calculated for $C_{10}H_8N_2S_2$.	Found.
Nitrogen	12.72	12.74

The crude product of the action of thiobenzoic acid on this substance was a varnish from which nothing solid was obtained. Thiobenzoic acid both with 1,2-propylene dithiocyanate, and 1,2,3-tripropylene thiocyanate also gave thick oils which were not further examined.

Benzal chloride and potassium thiocyanate, in alcoholic solution, gave a mixture of benzaldehyde and ethyl thiocyanate.

Methyldibromhydrocinnamate and Potassium Thiocyanate.—In the introduction it was mentioned that certain 2,3-dibromides react with potassium thiocyanate with the removal of bromine and formation of unsaturated compounds along with pseudocyanogensulphide. This peculiar reaction is well illustrated by the behavior of the dibromide obtained by adding bromine to methylcinnamate. Fifty grams of the dibromide were heated for eight hours with 40 grams of potassium thiocyanate, and 60 cc. of alcohol. In fact on simply mixing in the cold a yellow precipitate formed at once. This was extracted with water, alcohol, and carbon disulphide and then a nitrogen determination gave 24.65 per cent., while the analyses of various pseudocyanogen sulphide preparations, made by Goldberg, gave 22 to 27 per cent. nitrogen. On the other hand isopersulphocyanic acid contains 18.6 per cent. nitrogen.

The alcoholic solution was evaporated and the residue washed and taken up in petroleum ether, which left a small amount of substance undissolved. On evaporating, crystals sep-

arated melting at 33°, the melting-point of methyl cinnamate. This product was then distilled, and the boiling-point also agreed with that of methyl cinnamate. The yield after all this treatment was found to be 15 grams or 60 per cent. of the calculated.

The *dibromide from 2,4-dinitrostilbene* (15 grams), when boiled with alcoholic potassium thiocyanate, gave 6 grams of pure 2,4-dinitrostilbene or 64 per cent. of the calculated.

The *dibromide from the nitrile of phenyl cinnamic acid* (60 grams) gave 24 grams of the unsaturated product or 70 per cent. of the calculated. These yields do not represent the total amount of unsaturated material formed, since no special effort was made to obtain the entire amounts.

NEW HAVEN, CONN.,
February 10, 1902.

LIQUID MIXTURES OF MINIMUM BOILING-POINT.

BY CLIFFORD D. HOLLEY.

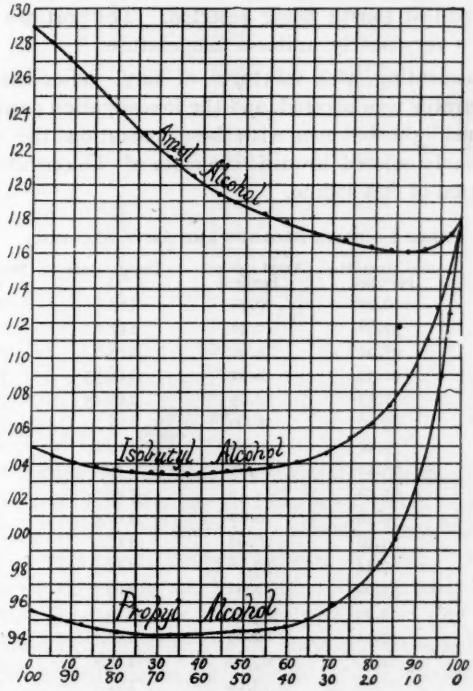
Received January 24, 1902.

IN 1899, Dr. Garnett Ryland[1] reported the results of an investigation of 80 pairs of the more common liquids. He found that 45 furnished mixtures which distilled in the same proportions with a constant boiling-point below the boiling-points of the constituent liquids; one which presented no relative depression or elevation of the boiling-point; and 3 which were of an uncertain character. During the same year, E. F. Thayer[2] and J. K. Haywood[3] investigated several of the same mixtures, but instead of following the method of Ryland, and determining the minimum-point by repeated distillations, they determined the boiling-points of several mixtures of the liquid constituents, and plotted the resulting boiling-point curve. From a comparison of the two methods it is seen that the proportion in which two liquids give a minimum point on the boiling-point curve is the same in which they distil with a constant boiling-point which lies below that of either liquid constituent, and the boiling-points are the same in both cases. But little having been done along this line during the past two years, it seemed desirable to add to our knowledge of such phenomena, and continue the investigations of such systems as would be likely to furnish mixtures of minimum boiling-point.

[1] *Am. Chem. J.*, **22**, No. 5.
[2] *Jour. Phys. Chem.*, **2**, 382; **3**, 32.
[3] *Ibid.*, **2**, 317.

In this paper are presented the results obtained with amyl compounds as one of the liquid constituents.

The boiling-point method was chosen as the more preferable, as in the distillation of bromides and iodides the formation of tarry residues towards the close of the distillation renders the thermometer readings inaccurate. A slightly modified form of Hite's apparatus was used. Instead of a differential thermometer,



one of the ordinary type was provided. It was graduated to fifths of a degree centigrade but with a scale so large that twentieths could be readily estimated.

A weighed amount of the lower boiling constituent was introduced into the bulb of Hite's apparatus, boiled for several minutes and the boiling-point and barometric pressure recorded. Weighed amounts of the other constituents were added, the successive boil-

ing-points noted, and this procedure was continued until the liquids were present in nearly equal proportions. The flask was then emptied and the process reversed, weighed portions of the first being added to a weighed amount of the second constituent. The results obtained are shown in the form of a plot. No corrections were applied to the curves because of variations of barometric pressure, as the error thus introduced is believed to be inappreciable. The liquids used were purified by redistillation, usually the first and last fourth being rejected. The portions reserved distilled at a very nearly uniform temperature.

In experimenting with mixtures of amyl iodide the bulb of Hite's apparatus was covered, and the investigation carried on in very subdued light, but even with these precautions the mixtures were noticeably colored towards the close of the operations from the separation of free iodine.

TABLE I.—AMYL BROMIDE AND AMYL ALCOHOL.

No.	Amyl bromide. Per cent.	Amyl alcohol. Per cent.	Temperature. °C	Barometer. mm.
1	100.00	0.00	117.9	764.1
2	97.68	2.32	117.2	764.1
3	95.04	4.96	116.8	764.1
4	91.39	8.61	116.35	764.0
5	87.33	12.67	116.15	764.0
6	83.40	16.60	116.3	764.0
7	79.22	20.78	116.4	764.0
8	73.12	26.88	116.8	764.0
9	65.58	34.42	117.25	763.9
10	59.38	40.62	117.9	763.9
11	53.98	46.02	118.4	763.9
12	47.44	52.56	118.9	763.8
13	43.00	57.00	119.5	763.8
14	43.29	56.71	119.0	763.8
15	37.91	62.09	120.3	763.8
16	32.40	67.60	121.5	763.8
17	26.86	73.14	122.7	763.7
18	21.03	78.97	124.0	763.7
19	17.32	82.68	124.9	763.7
20	13.28	86.72	126.0	763.6
21	9.02	90.98	127.0	763.5
22	4.23	95.77	128.1	763.5
23	0.00	100.00	129.0	763.4

TABLE II.—ISOBUTYL ALCOHOL AND AMYL BROMIDE.

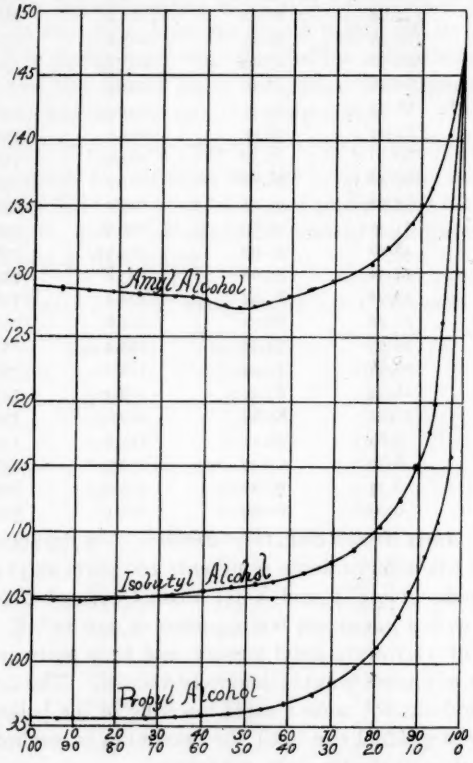
No.	Isobutyl alcohol. Per cent.	Amyl bromide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	105.0	757.8
2	94.88	5.12	104.3	757.8
3	89.50	10.50	104.0	757.8
4	84.33	15.67	103.8	757.8
5	79.92	20.08	103.65	757.8
6	76.35	23.65	103.6	757.8
7	72.96	27.04	103.55	757.5
8	69.36	30.34	103.5	757.5
9	66.63	33.37	103.45	757.5
10	63.63	36.37	103.4	757.4
11	60.70	39.30	103.45	757.4
12	57.48	42.52	103.5	757.5
13	54.56	45.44	103.6	757.5
14	51.37	48.63	103.7	757.4
15	48.10	51.90	103.75	757.4
16	44.32	55.68	103.8	757.4
17	38.08	61.92	104.1	757.4
18	31.28	68.72	104.6	757.3
19	25.55	74.45	105.4	757.3
20	20.56	79.44	106.2	757.3
21	16.55	83.45	107.4	757.3
22	12.22	87.88	109.0	757.3
23	7.89	92.11	111.2	757.2
24	6.01	93.99	112.9	757.0
25	2.73	97.27	115.0	757.0
26	0.00	100.00	118.1	757.0

Table I. Amyl Alcohol and Amyl Bromide.—In the accompanying plot the left-hand ordinate represents 100 parts amyl alcohol. Amyl bromide (117.9°) and amyl alcohol (129.0° C.) furnish a mixture with a minumum boiling-point of 116.15° C. in the proportion of 12.7 parts amyl alcohol, and 87.3 parts amyl bromide. The minimum point is definitely defined. The first additions of amyl alcohol cause a rapid lowering of the boiling-point followed by a gradual rise until the maximum is reached. The curve exhibits a distinctly wavy tendency.

Table II. Isobutyl Alcohol and Amyl Bromide.—Isobutyl alcohol (105°) and amyl bromide (118.1°) in the proportion of 63.6 parts isobutyl alcohol to 36.4 parts amyl bromide, gives a mixture having a minimum boiling-point of 103.4° C. The major portion of the curve is very flat, and the minimum point is not sharply marked. From the curve it is seen that isobutyl alcohol can be diluted with amyl bromide until it contains nearly 43 per cent. of

the latter before the boiling-point of the mixture is raised above that of isobutyl alcohol.

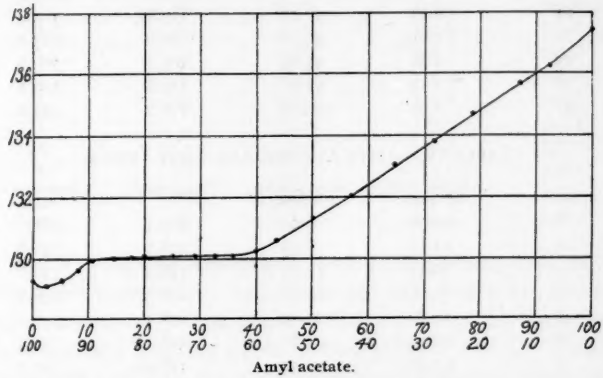
Table III. Propyl Alcohol and Amyl Bromide.—A mixture of propyl alcohol (95.5°), and amyl bromide (118.2°), in the proportions of 70.7 parts propyl alcohol to 29.3 parts amyl bromide, gives



a minimum point of 94°. The curve descends in a nearly straight line to the minimum, then rises very gradually at first, but at last with great abruptness to the maximum. Propyl alcohol may contain as much as 65 per cent. of amyl bromide without raising its boiling-point.

Table IV. Amyl Alcohol and Amyl Iodide.—Amyl alcohol

(128.9°) and amyl iodide (146.5°) furnish a mixture having a minimum boiling-point of 127.3° in the proportion of 52 parts amyl alcohol to 48 parts amyl iodide. The minimum point is



fairly well defined; the major portion of the curve is quite flat, and it is evident that amyl alcohol may contain as much as 65 per cent. of amyl iodide and still have a boiling-point below that of pure amyl alcohol.

TABLE III.—PROPYL ALCOHOL AND AMYL BROMIDE.

No.	Propyl alcohol. per cent.	Amyl bromide. per cent.	Temperature. °C.	Barometer, mm.
1	100.00	0.00	95.5	762.8
2	94.42	5.58	95.2	762.8
3	88.05	11.95	94.8	762.8
4	83.78	16.22	94.6	762.8
5	79.55	20.45	94.4	762.8
6	74.81	25.19	94.2	762.8
7	70.70	29.30	94.0	762.8
8	66.99	33.01	94.1	762.8
9	63.69	36.31	94.15	762.8
10	59.85	40.15	94.2	763.0
11	55.98	44.02	94.25	763.0
12	52.09	47.91	94.3	763.0
13	47.94	52.06	94.4	763.0
14	46.60	53.40	94.4	763.0
15	43.01	56.99	94.5	763.1
16	40.50	59.50	94.7	763.1
17	35.35	64.65	95.2	763.1
18	29.02	70.98	95.9	763.3
19	23.24	76.76	96.9	763.3

No.	Propyl alcohol. Per cent.	Amyl bromide. Per cent.	Temperature. °C.	Barometer mm.
20	18.23	81.77	98.3	763.3
21	14.81	85.19	99.6	963.4
22	11.38	88.62	101.6	763.4
23	8.77	91.23	103.85	763.4
24	6.49	93.51	106.2	763.6
25	4.36	95.64	109.1	763.6
26	2.14	97.86	112.6	763.6
27	0.00	100.00	118.2	763.6

TABLE IV.—AMYL ALCOHOL AND AMYL IODIDE.

No.	Amyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	128.9	758.6
2	93.57	6.43	128.6	758.6
3	87.47	12.53	128.4	758.6
4	81.19	18.81	128.3	758.6
5	74.80	25.20	128.2	758.6
6	70.19	29.81	128.18	758.7
7	67.46	32.54	128.05	758.7
8	63.26	36.74	127.9	758.7
9	60.08	39.92	127.7	758.6
10	56.18	43.82	127.4	758.6
11	51.98	48.02	127.3	758.6
12	48.89	51.11	127.4	758.7
13	45.84	54.16	127.6	758.0
14	40.48	59.52	128.0	758.0
15	35.60	64.40	128.6	758.0
16	30.32	69.68	129.3	758.1
17	21.28	78.72	130.6	758.1
18	18.12	81.88	132.0	758.1
19	12.64	87.36	133.7	758.1
20	10.10	89.90	135.2	758.1
21	7.43	92.57	136.5	758.3
22	3.16	96.84	140.5	758.3
23	2.04	97.96	142.3	758.3
24	0.00	100.00	146.5	758.3

TABLE V.—ISOBUTYL ALCOHOL AND AMYL IODIDE.

No.	Isobutyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	104.8	747.4
2	94.88	5.12	104.7	747.4
3	83.36	11.64	104.7	747.4
4	82.35	17.65	104.8	747.3
5	74.99	25.01	105.0	747.5
6	67.56	32.44	105.3	747.5
7	59.67	40.33	105.5	747.5

No.	Isobutyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
8	53.87	46.13	105.8	747.5
9	47.88	52.12	106.1	747.5
10	43.40	56.60	106.2	747.5
11	36.86	63.14	106.9	747.8
12	29.92	70.08	107.8	747.8
13	25.39	74.61	108.7	747.8
14	19.20	80.80	110.4	747.8
15	14.48	85.52	112.6	747.8
16	11.00	89.00	115.0	747.8
17	7.73	92.27	117.8	748.0
18	5.26	94.74	121.0	748.0
19	2.32	97.68	126.0	748.0
20	0.00	100.00	146.5	748.1

Table V. Isobutyl Alcohol and Amyl Iodide.—Isobutyl (104.8°) alcohol and amyl iodide (146.5°) do not give a mixture having a definite minimum boiling-point. The first two additions of amyl iodide caused a lowering of the boiling-point of 0.1° C. This was followed by a gradual rise until the mixture contained about 70 per cent. of amyl iodide, when the boiling-point rose with great abruptness to the maximum.

TABLE VI.—PROPYL ALCOHOL AND AMYL IODIDE.

No.	Propyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	95.7	753.8
2	93.36	6.64	95.6	753.8
3	89.94	10.06	95.65	753.8
4	79.91	20.09	95.7	753.8
5	73.06	26.94	95.8	753.8
6	66.16	33.84	95.9	753.8
7	59.90	40.10	96.1	753.8
8	54.38	45.62	96.3	753.7
9	46.15	53.85	96.6	753.4
10	41.08	58.92	96.9	753.4
11	36.50	65.40	97.6	753.4
12	30.27	69.73	98.4	753.4
13	24.90	75.10	99.7	753.4
14	19.19	80.81	101.4	753.4
15	14.78	85.22	103.4	753.5
16	11.48	88.52	105.6	753.5
17	8.64	91.36	108.2	753.2
18	5.95	94.05	110.8	753.2
19	3.07	96.93	115.6	753.2
20	0.00	100.00	146.5	753.2

TABLE VII.—AMYL ALCOHOL AND AMYL ACETATE.

No.	Amyl alcohol. Per cent.	Amyl acetate. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	129.3	770.4
2	97.36	2.64	129.1	770.4
3	94.58	5.42	129.3	770.4
4	91.84	8.16	129.55	770.4
5	89.10	10.90	129.9	770.4
6	85.42	14.58	129.95	770.3
7	82.06	17.94	130.0	770.3
8	78.48	21.52	130.0	770.3
9	74.80	25.20	130.05	770.3
10	71.27	28.73	130.01	770.3
11	67.62	32.38	130.01	770.1
12	64.16	35.84	130.1	770.0
13	60.08	39.92	130.2	770.0
14	56.87	43.13	130.5	770.0
15	50.04	49.96	131.3	769.6
16	42.88	57.12	132.0	769.6
17	35.21	64.79	133.0	769.7
18	27.83	72.17	133.8	769.8
19	20.85	79.15	134.55	769.8
20	17.80	82.20	135.5	769.9
21	7.49	92.51	136.2	769.9
22	0.00	100.00	137.5	770.0

Table VI. Propyl Alcohol and Amyl Iodide.—Propyl alcohol (95.7°) and amyl iodide (146.5) give results very similar to those obtained with isobutyl alcohol and amyl iodide. There is a slight lowering of the boiling-point, 0.1°, by the first two additions of propyl alcohol. The major portion of the curve is slightly flatter than with isobutyl alcohol and the abrupt ascent to the maximum more marked.

Table VII. Amyl Alcohol and Amyl Acetate.—Amyl alcohol (129.3°) and amyl acetate (137.5°) give a mixture having a minimum boiling-point of 129.1° in the ratio of 97.4 parts amyl alcohol to 2.6 parts amyl acetate. A second determination was made, and the same result obtained. The curve exhibits some marked peculiarities. There is at first a slight lowering of the boiling-point followed by a corresponding rise; the curve then becomes perfectly flat until the mixture contains 40 per cent. amyl acetate, when the curve rises in a straight line to the maximum.

The following pairs of liquids were investigated, but no mixtures of minimum boiling-point were obtained:

Amyl alcohol	129°	and ethyl butyrate	120.6°
Amyl alcohol	129°	and bromoform	147.1°
Amyl acetate	137.5°	and ethylene bromide	129°
Amyl acetate	137.5°	and amyl bromide	118°
Amyl acetate	137.5°	and amyl iodide	146.5°
Amyl acetate	137.5°	and bromoform	147.1°
Amyl acetate	137.5°	and ethyl butyrate	120.6°
Amyl bromide	118°	and ethyl butyrate	120.6°
Amyl bromide	118°	and toluene	109.5°

Of the 16 pairs of liquids investigated, 5 gave mixtures having well-defined minimum boiling-points, while 2 showed no relative elevation or depression of the boiling-point.

The chemical constitution of the constituents exercises a greater influence in the formation of mixtures with minimum boiling-points than the close proximity of the boiling-points of the constituents. One constituent remaining the same, or with constituents closely related, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

In the next paper the writer hopes to present the results obtained with propyl and isobutyl compounds.

UNIVERSITY OF MAINE.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE VOLUMETRIC ESTIMATION OF ALUMINA, AND FREE AND COMBINED SULPHURIC ACID IN ALUMS.

BY ALFRED H. WHITE.

Received January 25, 1902.

IN judging the quality of an alum, among the important determinations are those which give the amount of soluble alumina and the amount of sulphuric acid in combination with it or existing as free acid. The alumina may be satisfactorily estimated gravimetrically, but the method is tedious. A gravimetric estimation of the sulphuric acid gives not only that combined with aluminum plus that present as free sulphuric acid, but also that present as sodium sulphate, etc., and the amount of alkalies must be known before the amount of sulphuric acid combined with aluminum can be determined.

The determination of free sulphuric acid in alums by volumetric means has been repeatedly attempted. The hydrolysis of aluminum sulphate prevents direct titration with an alkali, since as fast as the free acid present is neutralized, more is formed by hydrol-

ysis, so that the solution will not remain neutral for an appreciable length of time until nearly all the acid originally combined with the aluminum has been neutralized, and most of the aluminum hydroxide precipitated. This cannot be made into a practicable quantitative method for the estimation of free and combined acid, as the formation of aluminate with alkaline reaction begins before all the hydroxide has been precipitated. Further if phenolphthalein is used as indicator the precipitated hydroxide obstinately holds, by adsorption, the pink color even when the solution is no longer alkaline so that the method, though perhaps giving in the hands of works chemists in constant practice results which are fairly concordant, is, because of these various errors, not to be considered a practicable analytical method. The following paper results from an attempt to work out a practicable method.

A standard solution of barium hydroxide was used instead of caustic soda to avoid any trouble caused by carbon dioxide in the caustic affecting the phenolphthalein used as indicator. It was found later that the barium hydroxide possessed other advantages. To prevent the adsorption of pink color by the precipitated aluminum hydroxide obscuring the end reaction, an addition of neutral potassium sodium tartrate (Rochelle salt) was made to hold the alumina in solution. The modification proved a good one. Duplicate results checked closely. There was no precipitation of alumina during the titration, nor even of barium sulphate. The solution remained perfectly clear and colorless until the end reaction, which was sharp. After standing a short time the solution became opalescent, and then milky, but no precipitate settled out. This marked retardation of the precipitation of barium sulphate was unexpected, and the conditions under which it occurs are undergoing further investigation.

To determine that the results thus obtained were accurate, a solution of aluminum sulphate was made by precipitating aluminum hydroxide from a solution of aluminum chloride with ammonia, washing the precipitate thoroughly and then dissolving in standard sulphuric acid which was afterward diluted to a liter (Solution A). The solution thus obtained was almost fifth-normal, and the amount of acid was slightly in excess of the amount theoretically necessary to form the normal aluminum sul-

phate. A duplicate solution of acid alone, carefully standardized gravimetrically, was used to check the results.

The method of procedure was as follows: To 25 cc. of the fifth-normal alum solution was added 50 cc. of 10 per cent. neutral potassium sodium tartrate, and the mixture was titrated cold with barium hydroxide solution, using phenolphthalein as indicator. This amount of tartrate was sufficient to prevent anything more than a slight opalescence in the solution before the end reaction. Duplicate titrations required 25.85 and 25.80 cc. of fifth-normal barium hydroxide. To determine the effect of the amount of tartrate, another titration was made, using 100 cc. of tartrate instead of 50. The amount of barium hydroxide solution used was 25.85 as before. The check solution of sulphuric acid required 25.65 cc. barium hydroxide, no difference being apparent whether no tartrate, 50 cc., or 100 cc. of tartrate were present. The solution containing the aluminum sulphate therefore requires slightly more barium hydroxide than that containing the sulphuric acid alone. A possible explanation is that the ionization of the barium hydroxide is lessened to such an extent by the aluminum tartrate complex that it requires an appreciably large excess of barium hydroxide to bring about the end reaction. If, however, the barium hydroxide is standardized against a solution of aluminum sulphate made from precipitated alumina and sulphuric acid as described, the results will be constant and give accurate results when extended to other alums. The addition of sodium sulphate in amount equivalent to the amount of sulphuric acid combined with the aluminum does not affect the result; the addition of standard sulphuric acid increases the amount of barium hydroxide used by the theoretical amount. The addition of neutral tartrate and titration with barium hydroxide, therefore, affords an accurate method of determining the total sulphuric acid combined with the aluminum plus the excess of free acid, irrespective of the amount of sulphuric acid combined with alkalies.

As it is well known that the hydroxy-organic acids in general have the power of preventing the precipitation of alumina, salts of other acids than tartaric were tried, among them neutral sodium citrate. Sodium citrate prevented the precipitation of alumina, retarded the precipitation of barium sulphate, and

allowed a perfectly sharp end reaction, as did the tartrate, but the amount of barium hydroxide used was only a little over two-thirds of that required when titrating in the presence of the tartrate. Solution A, with neutral sodium citrate added, required only 17.95 cc. barium hydroxide instead of 25.84 when tartrate was used. Experiment showed that the addition of sodium sulphate did not affect the result and that an addition of standard sulphuric acid caused the theoretically calculated increase in the barium hydroxide used. It seemed that the result obtained when titrating in the presence of citrate could be due only to the formation of a complex aluminum ion and that this might furnish the basis of a method for the estimation of the aluminum. If we assume that the barium hydroxide used when titrating in presence of tartrate, represents free acid plus acid combined with alumina, while the barium hydroxide used when titrating in presence of citrate represents free acid, plus two-thirds of acid combined with alumina, the difference represents one-third of the sulphuric acid combined with the alumina, or one-third the alumina. In the above instance, $25.84 - 17.95 = 7.89$ cc. fifth-normal barium hydroxide, and calculating the alumina on the assumption that this is equivalent to one-third of it we find that we get 0.0805 gram of alumina as compared with 0.0831 gram obtained gravimetrically. The volumetric result is too low. It seemed entirely possible that partial hydrolysis of the alum in the citrate solution might cause more barium hydroxide to be used than called for by the above supposition and that this might account for the low result. Accordingly, among other variations, the solution of aluminum sulphate was evaporated to dryness on the water-bath and dissolved in 50 cc. of 10 per cent. sodium citrate, and titrated. There were required only 17.58 cc. barium hydroxide instead of 17.95 cc., and the alumina calculated from this is 0.0842 gram instead of 0.0831 gram obtained gravimetrically. Using a saturated solution of citrate to redissolve the alum did not give an appreciably different result. Thus, the first method gives results considerably low while the second gives slightly high results. Some further experiments upon the influence of concentration and time follow, made upon a C. P. aluminum sulphate in a solution of 30 grams per liter (Solution B).

B.	Volume. Aluminum sulphate.	Water added.	Citrate added.	Barium hydroxide.	Remarks.
1	25	0	50	21.75	Titrated at once.
2	25	25	50	21.76	Titrated at once.
3	25	50	50	21.67	Water added; stood fifteen minutes; then citrate added, and titrated.
4	25	100	50	21.70	Water added; stood fifteen minutes; then citrate added, and titrated.
5	25	200	50	21.72	Water added; stood fifteen minutes; then citrate added, and titrated.
6	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate; stood ten minutes before titrating; required 21.62 cc. barium hydroxide.			
7	0.750 gram (25 cc.) of solid salt, dissolved in 50 cc. 10 per cent. citrate and titrated at once, required 21.90 cc. barium hydroxide.				

The above series of experiments shows that the addition of varying amounts of water and variation of time within short intervals makes but slight difference in the result. The hydrolysis is apparently a slow one. In twenty-four hours, however, equilibrium is practically complete, as is shown by another series of experiments on a commercial aluminum sulphate dissolved to a strength of 30 grams per liter (Solution C).

C.	Volume. Aluminum sulphate.	20 per cent. citrate added.	Barium hydroxide.	Remarks.
1	25	25	21.0	Titrated at once.
2	25	25	21.02	Stood fifteen minutes before titrating.
3	25	25	20.62	Stood sixteen hours before titrating.
4	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate.	20.53	Titrated at once.
5	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate.	20.69	Stood ten minutes before titrating.
6	0.750 gram (25 cc.) solid salt dissolved in 50 cc. 10 per cent. citrate.		21.10	Stood ten minutes before titrating.

Nos. 3 and 5 show that if sufficient time is given to allow equilibrium to be established, the results are practically the same

whether the 50 cc. solution is evaporated to dryness and dissolved in 50 cc. of 10 per cent. citrate (20.69 cc.) or 25 cc. of solution are treated with 25 cc. of 20 per cent. citrate, and the solution allowed to stand sixteen hours (20.62 cc.). No. 6 in this series, as well as No. 7 in Series B, shows that the same result is not reached when dissolving the solid salt in citrate (B 7 = 21.90) and titrating as when evaporating to dryness, and redissolving in the same amount of citrate (B 6 = 21.62). Commercial alum is evidently not a homogeneous body, and further combination between the alumina or basic sulphate and the sulphuric acid takes place after solution in water.

The analytical method as finally worked out is as follows: Dissolve 3 grams of alum in 100 cc. of water. Take 25 cc. sample, add 50 cc. strictly neutral 10 per cent. potassium-sodium tartrate and titrate with fifth-normal barium hydroxide, using phenolphthaleïn as indicator. This is equivalent to the sulphuric acid combined with the alumina plus the free acid. Evaporate a duplicate 25 cc. sample to dryness on the water-bath, dissolve in 50 cc. strictly neutral 10 per cent. sodium citrate, allow to stand ten minutes and titrate with barium hydroxide, with phenolphthaleïn indicator as before. The difference between these results is equivalent to one-third of the sulphuric acid combined with the alumina and hence to one-third of the alumina. The barium hydroxide solution should be standardized by a blank determination upon a solution of sulphuric acid in which approximately enough precipitated aluminum hydroxide has been dissolved to correspond to aluminum sulphate. The aluminum hydroxide may be best made by precipitation of the chloride to insure absence of sulphate. Caustic soda, even when freed from carbon dioxide by barium hydroxide, does not give such satisfactory results as the barium hydroxide. As examples of the practicability of the method the following results on two widely differing alums are cited.

Alum B, a C. P. aluminum sulphate:

30 grams per liter (25 cc.) sample = 0.750 gram sample.

		cc.
Fifth-normal barium hydroxide for tartrate titration	32.50 32.55	32.52
Fifth-normal barium hydroxide for citrate titration	21.60 21.63	21.62
Difference		10.90

10.90 × 3 = 32.70 cc. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina, and therefore equals alumina.

32.70 × 0.003407 = 0.1114 gram alumina equals 14.86 per cent. alumina. Alumina determined gravimetrically equals 14.73 and 14.80.

The close agreement between the figures 32.52 cc. (free and combined sulphur trioxide) and 32.70 cc. (combined sulphur trioxide) show that the alum is almost exactly neutral with an excess equal to 0.18 cc. of fifth-normal alumina.

Alum C, a commercial aluminum sulphate:

30 grams per liter (25 cc.) sample = 0.750 gram sample.

		cc.
Fifth-normal barium hydroxide for tartrate titration ...	33.59 33.59	33.59
Fifth-normal barium hydroxide for citrate titration	20.64 20.74	20.69
Difference		12.90

12.90 × 3 = 38.70 cc. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina and therefore equals alumina.

38.70 × 0.003407 = 0.1318 gram alumina equals 17.58 per cent. alumina. Alumina determined gravimetrically equals 17.57 and 17.50.

38.70 − 33.59 = 5.11 cc. fifth-normal alumina equals 0.0174 gram alumina equals 2.32 per cent. alumina more than is sufficient to form aluminum sulphate.

Alum B, as shown by the above figures, is slightly basic, but a determination of free acid by the method of Beilstein and Grosset[1] gave 0.9 per cent free acid. This method of Beilstein and Grosset has been investigated by V. Keler and Lunge,[2] who state that it gives results which are uniformly slightly high but otherwise very accurate, and it therefore became necessary to explain the discrepancy. The method of Beilstein and Grosset is as follows: Dissolve 1 or 2 grams of alum in 5 cc. of cold water, add 5 cc. of a cold, saturated solution of ammonium sulphate, allow to stand, with frequent stirring, for fifteen minutes, and then add 50 cc. 95 per cent. alcohol. Filter, wash with 50 cc. 95 per cent. alcohol, evaporate to dryness on water-bath, dissolve in water, and titrate with tenth-normal potassium hydroxide, using litmus as indicator. All the alum is, in this process, supposed to be precipitated as normal ammonium alum together with most of the excess ammonium sulphate, and the free sulphuric acid re-

[1] Bulletin de l'Academie Imperiale des Sciences in St. Petersburg, 1890, p. 147.

[2] *Zischr. angew. Chem.* (1894), p. 669.

mains in solution together with a small amount of ammonium sulphate. Three determinations of free acid in alum B by this method gave 0.86, 0.88, and 0.89 per cent. free acid as sulphur trioxide—as good an agreement as could be desired. To test whether an error in Beilstein and Grosset's method due to hydrolysis might not be responsible for this apparent free acid, variations were made in amount of water and concentration of sulphur trioxide, with the following results:

Sample. Grams.	Water. cc.	Saturated solution $(NH_4)_2SO_4$. cc.	Alcohol. Per cent.	Free acid as SO_3. Per cent.
2	10	10	95	0.96
3	10	10	95	0.88
3	5	10	absolute	0.70
3	5	5 + 5 gram solid ammonium sulphate.	absolute	0.61

Blank determinations showed that the change in results was not due to impurities in the ammonium sulphate or alcohol. The results show that the decrease in the relative amount of water decreases the apparent amount of free acid, but although hydrolysis does thus play a part in influencing the results, there remains as the lowest figure, 0.6 per cent., which can hardly be attributed to an error in the method. Turning back to the series of results obtained by titrating alum B in presence of citrate, it was remarked that the figures obtained by dissolving the alum directly in citrate were higher than those obtained by dissolving the alum in water, then evaporating to dryness and redissolving in citrate which showed a greater amount of free acid in the original alum than after evaporation to dryness. If the results in B 7 are taken and calculation made we find that there are required

	cc.
Fifth-normal barium hydroxide for tartrate titration.....	32.52
Fifth-normal barium hydroxide for citrate titration when alum dissolved directly in citrate.....	21.90
Difference.....	10.62

$10.62 \times 3 = 31.86$ cc.

$32.52 - 31.86 = 0.66$ cc. $= 0.70$ per cent. free acid as sulphur troxide.

This result is in fair accord with the results obtained by the Beilstein and Grosset method of direct estimation, and probably corresponds closely to the amount of free acid actually present in the solid salt. It is entirely incorrect, however, to hold that the

solution of this alum will have that amount of free acid, as the results on p. 463 show that the amount of alumina in solution is slightly greater than the amount necessary to form the normal salt. The solid salt is evidently not uniform. When dissolved in water to dilute solution, these inequalities disappear quickly. In concentrated solution, as in the Beilstein and Grosset method or when the salt is dissolved in citrate, equilibrium is attained much more slowly, and a titration of such a solution soon after solution is complete gives approximately the conditions prevailing in the solid salt. If the solution is allowed to stand a sufficient length of time, equilibrium is finally reached as shown by experiments C 3 and C 5, on page 461.

SUMMARY.

If a solution of an alum to which has been added neutral potassium sodium tartrate (Rochelle salt) is titrated with barium hydroxide, the barium hydroxide used will correspond to the sulphuric acid combined with the alumina plus the free acid. The sulphuric acid combined with sodium or potassium is not estimated. If a duplicate solution of alum is evaporated to dryness, redissolved in neutral sodium citrate and titrated with barium hydroxide, a smaller quantity of barium hydroxide is required, and the difference between the amounts of barium hydroxide used in the two titrations is equivalent to one-third of the alumina. From these two titrations can be calculated the alumina and the sulphuric acid combined with it whether the alum be basic or acid, and if the alum is acid, the excess of acid over that necessary to form the normal sulphate. Commercial aluminum sulphate may, in its solid state, carry free acid, although in the solution such uncombined acid may disappear, combining with what had been basic portions of the solid salt. Such free acid may be estimated by dissolving the solid salt directly in citrate and titrating with barium hydroxide at once. This method gives results closely concordant with Beilstein and Grosset's method, but it does not show that the alum contains more acid than is sufficient to form with the alumina the normal salt.

When aluminum sulphate is titrated with barium hydroxide thus, in presence of neutral alkali tartrate or citrate, the precipitation of barium sulphate is retarded for a time, varying from a few minutes to several hours and when the precipitate does form it is in a very peculiar colloidal form which is undergoing further

investigation. Consideration of this subject and also of the action of salts of other metals than aluminum and salts of other acids than tartaric and citric, as well as the theoretical points involved are reserved for a following paper.

ANN ARBOR, MICH.,
December, 1901.

THE ANALYTICAL CONSTANTS OF NEATSFOOT, TALLOW AND HORSE OILS.

BY AUGUSTUS H. GILL AND ALLAN W. ROWE.

Received February 3, 1902.

OF the commonly occurring oils, fewer data are to be found about these three than about any of the others; this work was undertaken to supply this need.

The various tests were applied as described in a book published by one of us;[1] that is, the specific gravity was taken with a correct Westphal balance at 15° C. or 100° C.; the Valenta test was done with an equal quantity of glacial acetic acid, proved to be 100 per cent. by titration; the Maumené test was performed with 100 per cent. sulphuric acid, its strength also determined by titration, in a jacketed beaker, the acid being run into the oil drop by drop from a burette; the iodine number, with the solutions after having been mixed twenty-four hours, and the oils allowed to stand for four hours with it. The titer test was carried out as prescribed by Lewkowitsch, the acid being melted in a 5″ test-tube held in a 100 cc. round-bottomed flask. The results given are usually the average of two closely agreeing determinations. The oils used were obtained from different dealers and guaranteed pure.

The constants are as follows:

	Sp. gr. 15° C.	Valenta. °C.	Maumené. °C.	Sp. temp. reaction.	Iodine. No.	Titer test. °C.	Iodine No fatty acid
Neatsfoot oil, 1	0.915	70.0	42.2	87.9	72.9	19–20	68.6
" " 2	0.914	75.5	42.2	87.9	72.9	18–19	64.6
" " 3	0.919	51.0	49.5	103.1	67.1	17–18	67.3
" " 4	0.916	61.5	42.2	87.9	72.1	16	69.5
" " 5	0.916	75.5	42.2	87.9	66.0	25.5–26.5	63.6
Usual figures ...	0.915	....	48.0	....	70.0	26.0	....
	100° C.						
Tallow oil, 1	0.794	73.5	35.0	72.9	55.8	35–36	54.6
" " 2	0.794	71.0	35.0	72.9	56.6	36.5–37.5	57.0
" " 3	0.794	75.7	35.0	72.9	56.7	34.5–35.5	56.6
	15° C.						
Usual figures ...	0.916	47.0	43.0	....	57.0	39	....

[1] Gill: "A Short Handbook of Oil Analysis."

Horse oils and fats.	Color, etc.	Sp. gr. at 15° C.	Valenta. °C.	Maumené. °C.	Sp. temp. reaction.	Iodine No.	Iodine No. of clear oil.	Titer test. °C.	Iodine No. of fatty acids.
1	White-brown semi fluid	0.919	80.2	46.0	95.8	75.1	....	32.5–33.5	72.9
2	Dark brown semi liquid	0.916	54.0	52.1	108.5	82.5	82.0	30.0–31.0	72.3
3	Yellow-brown liquid	0.922	71.0	54.7	114.0	86.3	83.7	25.0–26.0	78.7
		100° C.							
4	Golden brown nearly solid	0.798	48.0	54.2	112.9	79.9	81.8	30–31	80.4
5	Very like, 4	0.799	61.0	53.5	111.5	78.8	78.2	34–35	82.1

Neatsfoot oils: the samples are fairly concordant with the exception of No. 3; the gravity and Maumené test are higher than those of the others; as no adulterant could be proved, it is supposedly genuine.

Tallow oils: the results here, upon oils from different sources, are remarkably concordant.

Horse oils: as was expected from their different appearance, these show a considerable variation; the Valenta test is of no use whatsoever here; No. 5 came from a young horse; nothing is known about the others.

Were either of these oils used to adulterate neatsfoot, the horse oil would raise the Maumené and iodine values, and the titer test; tallow oil would lower the Maumené, and iodine values, and raise the titer test quite considerably.

A TEST FOR THE GUMMING QUALITY OF LUBRICATING OILS.

By Augustus H. Gill.

Received February 3, 1902.

SOME years ago in studying the Elaïdin test for oils, a few of the mineral lubricating oils were included, and it was noticed that those which deposited the most "tar" apparently changed the most in use. The test, other than a repetition with different oils, lacked confirmation as to its value except in one case. It was noticed that with a 25° paraffin oil the outside of the can containing it—where it was exposed to the air in thin layers—was covered with a skin closely resembling that produced

by linseed oil. The object of this work was to show that there is a connection between the amount of change ("tar") and the quantity of oxygen absorbed. The gumming test was applied after the manner of the Elaïdin test by treating 5 grams of the oil in a cordial glass with 11 grams of Roth's liquid (nitrosulphuric acid) the two being thoroughly stirred together and cooled by immersion in a pan of water at 10°–15° C. Brownish spots or, in case of a bad oil, masses form around the edges and become red in the course of two hours. The nitrosulphuric acid is prepared by saturating sulphuric acid of 46° Bé., containing a few drops of nitric acid, at 0° with nitric oxide.

The quantity of oxygen absorbed was determined by sealing 5 to 10 grams of the oil in a flask and heating it to 80°–105°, the flask being occasionally shaken. The oil was weighed into the flask, care being taken that none touched the neck; the neck was drawn down to a long thin-walled capillary, the flask allowed to cool at 20°, and then quickly sealed in a small blast-lamp flame. After heating about 100 hours the flask was allowed to cool to 20°, the capillary broken under water and the inflowing water weighed. This represented the number of cubic centimeters of oxygen absorbed from the air. The results are shown in the table. It was thought that possibly a difference between these oils might be shown by either the bromine, iodine or Maumené tests: the differences were, however, so slight as to show that these could not be used as a means of distinguishing between the oils.

The results should be compared crosswise of the table, as the temperatures, time of exposure, and amount of shaking varied with each test. With the engine oils the amount of tar formed seems to bear a close relation to the quantity of oxygen absorbed; this does not apparently hold true of the spindle oil tested.

	1.	2.	3.	4.
Name of oil.....	25° paraffin.	Red lubricating.	No 1 engine.	No. 1 spindle.
Appearance in gumming test.....	Dark brown pitchy cake.	Some dark pitch.	Dark brown, trace of pitch.	Medium brown, no pitch.
	cc.	cc.	cc.	cc.
Oxygen absorbed per 100 grams oil at 80°.....	45.6	60.0	12.2	36.0
	46.0	62.3	13.0	41.5
Oxygen absorbed at 80°–85°, 12 days.....	190.5	....	34.1	159.5
	180.0	....	....	160.9
	105.4	121.0	35.6	54.6
	101.6	....	36.4	50.4
Oxygen absorbed at 98°–115°, 12 days.....	....	427.0	111.0	321.0
	....	402.0	104.0	320.0
Oxygen absorbed at 95°–105°, 12 days.....	188.0	238.0	65.0	251.0
	170.0	272.0	....	....

ANALYSES REQUIRED FOR AN ELECTROLYTIC ALKALI WORKS.

By J. H. James and J. C. Ritchey.

Received February 15, 1902.

WHILE in the main the analytical methods for an electrolytic alkali works are the same as used in the old processes of caustic and bleach manufacture, we have found in practice that the modifications given below facilitate the operations required. Some of the analytical methods necessarily have to be varied from those of the old processes because of the inherent difference in the electrolytic method of manufacture.

The analyses given below, which are used for a plant working a mercury cathode process, may be discussed under the following heads: (1) Raw Materials; (2) Factory Control; (3) Finished Products.

RAW MATERIALS.

Limestone.

Determinations: Silica, ferric oxide and alumina, calcium carbonate, magnesium carbonate. These determinations are carried out in the usual way. A limestone as high as possible in calcium carbonate is required.

Slaked Lime.

Determinations: Water and carbon dioxide.

Water.—The workmen in the lime house become so expert in the slaking that they can generally tell by the physical characteristics when just enough water has been added, hence a water determination is not often required. When a sample comes to the laboratory it is quartered down quickly to about one ounce, and one gram heated for one hour over a blast-lamp. The loss in weight is reported as total water.

Carbon Dioxide.—This is rarely determined and usually amounts only to one- or two-tenths of a per cent. The determination is made in the usual manner with a Schroetter or other apparatus used in the analysis of carbonates.

Salt.

Determinations: Insoluble in water, calcium sulphate ($CaSO_4$, $2H_2O$), calcium chloride ($CaCl_2$,$6H_2O$), magnesium sulphate ($MgSO_4$), magnesium chloride ($MgCl_2$,$6H_2O$), sodium sulphate (Na_2SO_4), ferric oxide and alumina, and sodium chloride.

We make the analysis on the sample which has been dried over night in the steam oven at 100° to 105° C., and calculate the above salts according to the laws for the distribution of acids and bases, the determinations being ferric oxide and alumina, lime, magnesia, sulphur trioxide, and chlorine. Since the ferric oxide and alumina are usually very small in amount, they are not regarded in the distribution of acids and bases, but reported as weighed.

A salt low in sulphates and lime salts is required, as these accumulate and foul the electrolyte.

Water.

Determinations: Total solids and complete analyses of inorganic constituents. These determinations are made in the usual manner. A water low in sulphates and lime salts is required for the same reason as above.

FACTORY CONTROL.

Caustic Liquor.

Determinations: Sodium hydroxide and sodium chloride. Five cc. of the liquor as it comes from the cell is taken, the alkalinity determined by normal sulphuric acid with phenolphthalein as indicator, then a few drops of neutral potassium chromate solution are added and the sodium chloride determined by decinormal silver nitrate.

In this way, individual cells tests are made once each day and a test on the average liquor from each unit of forty cells is made every two hours throughout the twenty-four.

Spent Brine.

Determinations: Specific gravity at 60° F., free chlorine, sodium hypochlorite, sodium chlorate, sodium chloride, sulphur trioxide, iron and aluminum oxides, lime, magnesia and mercury. About one liter of the brine is required for the tests. The results are reported in grams per liter.

Specific Gravity.—The specific gravity is best determined by cooling a portion of the brine to 60° F., and taking the reading with a Westphal or Mohr balance.

Free Chlorine.—Pipette out two portions of brine of 50 cc. each into 8-oz. Erlenmeyer flasks, add 10 cc. of a saturated solution of potassium iodide, shake well, stand five minutes, titrate the lib-

erated iodine with decinormal hyposulphite, using starch solution as indicator. Multiplying the number of cubic centimeters "hypo" solution required by 0.00355 × 20 gives the number of grams of free chlorine per liter.

Sodium Hypochlorite.—Two portions of brine of 50 cc. each are pipetted into 200 cc. beakers and the free chlorine + sodium hypochlorite determined with decinormal arsenious acid (Penot's method), using drops of starch solution and potassium iodide on a spotting plate as indicator. Deduct from this the number of cubic centimeters of "hypo" required for the free chlorine, and multiply the remainder by 0.003724 × 20, which gives the number of grams of sodium hypochlorite per liter.

Sodium Chlorate.—For this determination we prefer the following modification of the method given in Sutton's "Volumetric Analysis."

Take either the solutions from the sodium hypochlorite titration or pipette out two portions of 50 cc. each into 8-oz. Erlenmeyer flasks, and run in the number of cubic centimeters decinormal arsenious acid solution as determined above. Weigh out a quantity of C. P. ammonium ferrous sulphate in excess of the chlorate (unless it is known about how the brine is running in chlorate, several trials may be required to find this weight). Add the ferrous salt to the solution in the Erlenmeyer flask, close the mouth of the flask with a small funnel and place on a hot plate or sand-bath. Add 15 cc. concentrated sulphuric acid through the funnel (about 1 cc. at a time) slowly, allow to come to a gentle boil and remain so for three or four minutes. Then cool the solution and titrate the excess of ferrous salt with potassium bichromate. Multiply the amount of ferrous iron present by 7 to obtain the weight of ammonium ferrous sulphate in excess. Deducting this from the amount weighed out gives the ferrous salt oxidized by the chlorate decomposition, and this multiplied by 25.51 × 0.001775 × 20 = number of grams of sodium chlorate per liter, or the same result is obtained by multiplying the weight of iron oxidized by 0.3169 × 20.

Sodium Chloride.—Instead of making the titration for sodium chloride in the same solution in which the chlorates were determined, as recommended by Sutton, we find it quite as accurate and more rapid to proceed as follows: Take 50 cc. of the cooled solution just after reading the specific gravity, and dilute to 1

liter with distilled water. Pipette out portions of 10 cc. each and titrate with decinormal silver nitrate, using about 8 drops of a 10 per cent. solution of neutral potassium chromate as indicator. Multiply the reading in cubic centimeters by 100, deduct from this the number of cubic centimeters of arsenious acid solution required in the free chlorine + sodium hypochlorite titration, which is a sufficiently accurate correction for the free chlorine and sodium hypochlorite present; the remainder multiplied by 0.00585×20 gives the number of grams of sodium chloride per liter.

Sulphur Trioxide.—Pipette out 2 portions of 50 cc. each, add to each 50 cc. water with 3 cc. concentrated hydrochloric acid, and boil violently to completely decompose all hypochlorites and chlorates. When the smell of chlorine has disappeared, add slowly to the boiling solution 10 cc. of saturated barium chloride solution which have been diluted to 50 cc. and heated to boiling. Allow to stand until the precipitate settles, filter, wash with hot water to free precipitate from chlorides, dry, ignite, and weigh barium ulphate, and from this, calculate the sulphur trioxide.

Ferric Oxide and Alumina, Lime, and Magnesia.—Two portions of 100 cc. each are pipetted out, 50 cc. water with 3 cc. concentrated hydrochloric acid added to each, and the solutions then boiled violently until the smell of chlorine has disappeared. The precipitation and weighing of ferric oxide and alumina, the determination of the lime, and the precipitation and weighing of the magnesia are conducted the same as in an ordinary limestone analysis.

Mercury.—Two portions of 50 cc. each are pipetted out, 50 cc. of water with 3 cc. concentrated hydrochloric acid added to each, and the solutions boiled violently for several minutes. When the smell of chlorine has disappeared, pass hydrogen sulphide through the hot solution until the mercury is all precipitated. Filter on a Gooch filter that has been previously dried at 100° C. for one hour and weighed. Wash the precipitated mercuric sulphide with hydrogen sulphide water until all the sodium chloride is removed, then with alcohol, next with ether, then with carbon bisulphide until all the free sulphur is removed. Finally wash out the carbon bisulphide with ether, then follow with alcohol, dry at 100° C. for one hour and weigh as mercuric sulphide. Calculate to mercury and report as such.

A complete analysis of the spent brine as above is made each week on a sample which represents an average of all the cells. Individual cell tests on the brine for sodium chloride alone are made once per day. A complete brine analysis with the exception of the magnesia can be made by one chemist in about four hours. The magnesia, precipitated as ammonium magnesium phosphate, is allowed to stand over night and finished the next morning.

Chlorine Gas.

Determinations: Chlorine and hydrogen.

These tests are made with an ordinary Orsat-Muencke gas analysis apparatus, having two pipettes filled with a solution of potassium iodide and caustic potash which serve for the chlorine absorption (the small amount of carbon dioxide gas present is negligible), while a palladium tube is attached for absorbing the hydrogen.

These tests are made on the gas once each day.

FINISHED PRODUCTS.

Caustic Soda.

Determinations: Sodium hydroxide + sodium carbonate, and sodium chloride (other determinations to make a complete analysis are rarely asked for).

The sample, which usually comes to the laboratory still hot, should be taken from the bottle, piece by piece, and broken quickly in a mortar to pieces no larger than a pea, bottling again as quickly as possible. When all is broken, mix sample thoroughly by turning the bottle over and over. The bottle should not be more than two-thirds full to insure a thorough mixing. Take a weighing bottle, which has been previously dried and weighed, and fill it with caustic from the mixing-bottle, close bottle, and reweigh. Empty the caustic from the weighing-bottle into a beaker, dissolve and pour caustic solutions and rinsings into a liter flask. Dilute nearly to the mark, cool under the tap to a temperature approximately that of the room, dilute to the mark, mix thoroughly by turning the stoppered flask end over end.

Sodium Hydroxide + Sodium Carbonate (Total Na_2O).—Pipette out 50 cc. of the caustic solution into a beaker, add 4 or 5 drops of methyl orange indicator and titrate with normal sulphuric acid.

Repeat the titration on 50 cc. portions until a constant reading is obtained. Multiply the number of cubic centimeters used by 0.031 × 20 and divide by the weight of caustic taken; this gives the per cent. of total Na_2O in the sample, *i. e.*, the Na_2O existing as carbonate and hydroxide, the small amount existing as sulphide and sulphite, etc., being disregarded.

Sodium Chloride.—Pipette out two cc. portions of the caustic solutions into beakers of 250 cc. capacity, carefully neutralize with nitric acid, and titrate the sodium chloride with decinormal silver nitrate as usual.

The caustic soda analysis is usually limited to a determination of the total Na_2O, which is made on a sample from each pot as it is finished.

Bleaching-Powder.

Determinations: Available chlorine, water, carbon dioxide, total chlorine.

Available Chlorine.—This test is best made by the old arsenious acid titration (Penot's method).

Water.—We have been unable to find a perfectly satisfactory method for this determination, but have used the following:

One gram of the bleaching-powder is quickly mixed with about 5 grams of dry copper oxide and placed in a porcelain boat near the back part of a 12-inch combustion tube. Beyond the boat the tube is filled with scrap sheet silver mixed with cement silver which should be in a spongy condition. A weighed Geissler bulb containing sulphuric acid is attached for absorption of the water. Two similar bulbs are attached at the other end for drying the air which enters the tube. The tube is heated gently at first, dry air being aspirated slowly through the apparatus, finally the heat is raised immediately under the boat as high as the tube will stand and kept so for an hour and a half. The sulphuric acid bulb is detached and weighed in the usual manner.

This method of retaining the chlorine is based on the following reaction:[1]

$$Ca(OCl)_2 + 4CuO = CaCl_2 + 2O_2 + 2Cu_2O.$$

The silver serves to retain any chlorine that may escape from the boat.

Carbon Dioxide.—For this determination a train was arranged

[1] Richter's "Inorganic Chemistry," p. 370.

as follows: First, two potash bulbs for removing the carbon dioxide from the air entering the apparatus; second, a flask of about 100 cc. capacity fitted with a stop-cock funnel for introducing the acid for decomposition; third, three Geissler bulbs filled with a nearly saturated potassium iodide solution for absorption of the evolved chlorine; fourth, a U-tube containing fused calcium chloride lumps free from caustic for absorption of water from the gas before it enters the potash bulb; fifth, a weighed potash bulb for the absorption of the carbon dioxide.

One gram of the bleaching-powder is placed into the decomposition flask and about 15 cc. of dilute hydrochloric acid (1:4) dropped in from the stop-cock funnel, a current of air being slowly aspirated through the apparatus. The chlorine is all absorbed in the first and second potassium iodide bulbs, the third remaining colorless. To remove the carbon dioxide that is absorbed by the potassium iodide solution, the aspiration of the air is continued for two hours after the bleaching-powder is decomposed. While there is a possibility of iodine vapor being carried over into the potash bulb, we have had no such trouble as the third potassium iodide bulb, remains colorless throughout the operation. The potash bulb is detached and weighed in the usual manner.

Total Chlorine.—One-half gram of the bleaching-powder is reduced with arsenious acid solution as in the available chlorine test, then neutralized with nitric acid and the chlorine determined in an aliquot part with decinormal silver nitrate solution; this gives the chlorine existing as hypochlorite and chloride. A determination of the chlorates present by the method under spent brine analysis, is made on one-half gram of the sample. It is better, however, to use hydrochloric acid for the chlorate decomposition here. For these results the total chlorine is calculated.

Of the above determinations, the available chlorine is the only one made in daily practice. This analysis is made on the chamber that is "up to strength" just before the charge is withdrawn for packing.

Nearly all the above analyses are made at this laboratory for Mr. B. E. F. Rhodin, managing director of the Canadian Electro-Chemical Co., to whom we are indebted for many suggestions and courtesies.

THE LABORATORY OF THE LAKE SUPERIOR POWER CO., SAULT STE. MARIE, ONTARIO.

BURETTE ARRANGEMENT.

By E. M. Johnson.

Received February 15, 1902.

THE burette arrangement here shown has been found very satisfactory and convenient in a metallurgical laboratory where a number of standard solutions are in use every day. The glass tube *B* is connected direct to the three-way burette by a short rubber tube *A*. This connection should be made so as to bring the ends of the glass tubes very near to each other, practically doing away with any contact between the standard solution and the rubber. There is no pressure on the rubber connection, consequently no leakage, as is the case when the burettes are filled by force of gravity. The burette is held in place by an ordinary bird cage spring *C*, and can be easily detached and cleaned by disconnecting the connection *A* and unhooking the spring. It is easier to replace an empty standard solution bottle than is the case with other devices. This is done by simply disconnecting at *A* and running the glass tube *B* up high enough to put in a full bottle. The glass tube *B* should slide with ease through the rubber stopper. The surface of the glass plate next to the table may be painted white, or some suitable white material placed under it. It is very easy to keep the glass plate clean.

Denver, Colorado,
February 12, 1902.

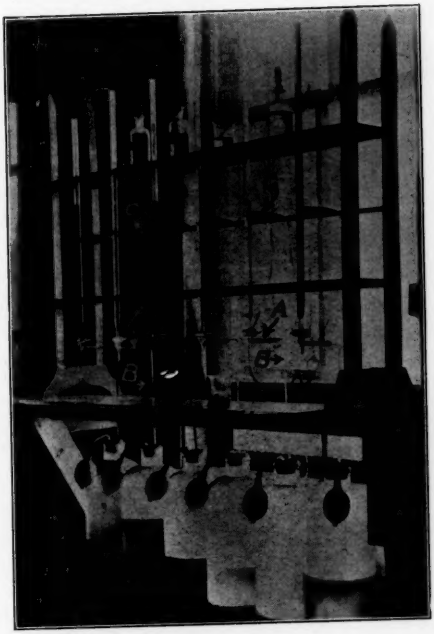
A GENERATOR FOR HYDROGEN SULPHIDE.

By J. N. Swan.

Received January 20, 1902.

OF the making of apparatus for the generation of hydrogen sulphide there is no end. One would think that out of the more than 200 acetylene generators on the market a machine might be chosen which would at least approximate perfection as a generator for hydrogen sulphide. If one generates the gas on the large scale and uses a gasometer with pipes leading to the places where the gas is to be used there are machines which give satisfactory results. If, however, it is desired to use the gas in fairly small quantities as, *e. g.*, with an ordinary class in qualitative analysis, there is still something to be desired in the way of a machine that will give satisfactory results in every particular.

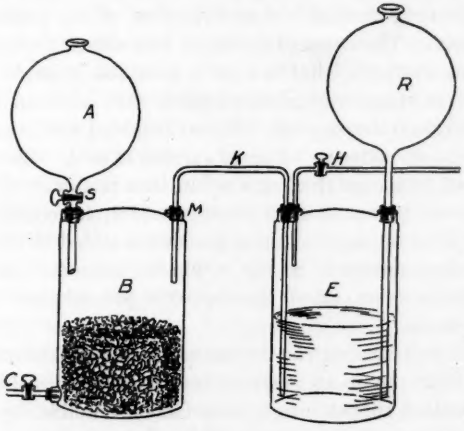
The machine herewith illustrated has been used for such work



in this laboratary with better results than had been obtained before, using a number of different forms of generators. The generator was made by assembling ordinary laboratory apparatus.

Referring to the figure, a two-necked Woulfe flask, *B*, contains the iron sulphide. Into one neck is fitted a separatory funnel, *A*, with a stop-cock, *S*. This funnel contains the dilute acid. *E* is a second two-necked Woulfe flask. Into one of the necks of this flask a tube, *R*, is fitted so that it reaches nearly to the bottom of the flask. The upper part of this tube contains a large bulb. The inner part of a Kipp apparatus is a good tube for the purpose. A tube, *K*, connects the two flasks and terminates under the water with which *E* is partly filled. An exit tube, *H*, with a stop-cock, forms the tube which delivers the gas ready for use.

To generate the gas, the stop-cock *S* is turned and a small quantity of the dilute acid is allowed to trickle down upon the sulphide in the Woulfe flask. As the gas is generated it passes through *K* into the flask *E*, in which passage it is washed by



bubbling up through the water in *E*. At the same time the pressure of the gas collecting in *E* will force the water up into *R*. By turning the stop-cock *H*, a supply of gas is received under the pressure of the head of water in *R*. If an excess of acid is permitted to flow out of the separatory funnel the gas generated by it will be stored in *E* ready for the next time it is to be used.

The spent acid can be removed at *C* at any time, and the flask

B thoroughly washed out by disconnecting at *M*, and allowing a stream of water to flow through the flask. This can be done without disturbing the acid in *A*. When fresh water is put into *E*, sufficient gas to saturate the water should be passed into it slowly if the machine is to stand for any length of time before being used. This will prevent the water from running back into *B* on standing.

It is probable that the chief advantage in this form of machine is that there are no narrow tubes to become clogged with salts crystallizing from the spent acid. In actual practice it has been found that there is a minimum amount of gas wasted and a maximum amount of time saved in caring for the machine as compared with other machines in common use.

MONMOUTH, ILLINOIS.

THE DETERMINATION OF COPPER BY ALUMINUM FOIL.

BY GEORGE E. PERKINS.

Received February 7, 1902.

THE following method is a modification of the process by A. H. Low. The copper is brought into solution as a sulphate by treatment similar to that in Low's modified cyanide process. The solution is evaporated until all nitric acid has been driven off and dense white fumes appear. Water is added until the dilution is about 50 cc. of water to 10 cc. of sulphuric acid. Sheet aluminum of about 25 gauge thickness is cut into pieces about 40 mm. square with one corner of each piece turned up for convenience in handling. Two or three of these pieces are added to the beaker containing the solution of copper. The solution is then boiled. In about five minutes, all of the copper is precipitated upon the aluminum sheets.

Instead of redissolving the deposited copper and titrating with cyanide solution, more satisfactory results are obtained by washing the deposited copper into a tared Gooch crucible, by giving a final wash with alcohol and by burning off the alcohol and drying. Weigh the result as metallic copper.

In forming the filter, care should be taken that only sufficient asbestos fiber is used to produce a good filter. In washing with alcohol and burning, the same care is needed as in the electrolytic method that too much alcohol is not used.

PROVIDENCE, R. I.,
February 3, 1902.

[1] Read before the January meeting of the Rhode Island Section of the American Chemical Society.

SUPPLEMENTARY NOTE TO A "GRAVIMETRIC METHOD FOR THE ESTIMATION OF HYDROGEN DIOXIDE."

By George E. Hosch.

Received February 28, 1902.

IN This Journal, **23**, 923, the author describes a method for determining the strength of hydrogen dioxide by the use of a "Schrötter" alkalimeter. Upon further experiment, he finds that a Geissler style modified by Dr. Shepard with removable parts, is a more convenient form, especially where a number of assays are to be made in succession. When the decomposition is complete, and if the apparatus is aspirated for about three minutes with air which had been previously dried by calcium chloride, the results obtained are much more satisfactory. A saturated filtered solution of bleaching-powder may be substituted for the potassium permanganate, as already suggested, but instead of dilute sulphuric acid a weak solution of caustic soda must be used in the bulb, and as in the case of permanganate, divide the results obtained by 2. But the most consistent results may be obtained by employing a filtered saturated solution of lead acetate as a decomposing substance for the hydrogen dioxide. As this is a catalytic action (all the oxygen generated comes from hydrogen dioxide itself), one may operate upon as much as 5 cc. of the hydrogen dioxide, but this precaution must be observed ; in working with commercial samples or those which contain much free acid, a weak solution of caustic soda should be used in the bulb, as in the case of the bleaching-powder. The following tables are the results (in per cent.) obtained from pure and commercial samples of hydrogen dioxide, employing the different decomposing substances, just mentioned :

MEDICINAL SAMPLE, 0.05 PER CENT. FREE ACID (HCl).

	$Pb(C_2H_3O_2)_2$.	$Ca(ClO)Cl$.	$KMnO_4$.	$KMnO_4$ volumetric.
	3.01	2.95	3.30	....
	2.98	2.99	2.86	....
	2.99	3.00	3.11	....
Average,	2.99	2.98	3.09	3.01

COMMERCIAL SAMPLE, 0.91 PER CENT. FREE ACID (H_2SO_4).

	1.01	0.93	1.07	....
	1.05	1.03	1.09	....
Average,	1.03	0.98	1.08	1.05

NEW BOOKS.

ELEMENTARY ELECTRICITY AND MAGNETISM. By DUGALD C. JACKSON, E.E., Prof. of Electrical Engineering, University of Wisconsin, and J. P. JACKSON, M.E., Prof. Electrical Engineering, Penna. State College. The Macmillan Company.

This volume will be appreciated by all persons who wish to acquire some knowledge of the subjects it presents. While the authors have written in an elementary way, every topic is as scientifically and exhaustively discussed as one would expect from an expert. In these days when electricity is applied so extensively, and when many employ it without adequate previous training as to its origin, its control, measurement, etc., the present volume comes as a reliable and trusty handbook. To chemists, who have not enjoyed a full training in physics, it cannot fail to recommend ifself. It is well written and well illustrated.

EDGAR F. SMITH.

ENZYMES AND THEIR APPLICATION. By DR. JEAN EFFRONT, translated by S. C. PRESCOTT. Published by John Wiley & Sons, New York.

The interest in enzymes is growing very rapidly. The sphere of their application is largely increased both in theoretical and industrial chemistry. Biology is probably the science that has profited most from the study of enzymes, and many problems that were in darkness for decades lose their mysteriousness in the light of the new discoveries of certain functions of enzymes.

But the results of all the new investigations were never summed up in a systematic, brief and popular form. Prof. Effront's book supplied that gap in the chemical literature, and Mr. Prescott's translation of the work under the title "Enzymes and their Application" will be welcomed by all interested in the subject.

The present volume deals chiefly with the enzymes of the carbohydrates, and briefly with the oxidases. In the following volume the proteolytic enzymes and toxines will be discussed.

The book being a summary of a course of lectures delivered at the Institute of Fermentation at the University of Brussels, it naturally has a more or less elementary character, and cannot be regarded as a reference or text-book. But all the greater is its value for one who seeks a general knowledge on the subject both from theoretical and practical standpoints. The theoretical problems are discussed in a very clear and comprehensive way. The

introductory chapter on the synthetic and analytic work of the living cell is perhaps a little too brief, but the question of the "Manner of Action of Diastase" is discussed exhaustively in the light of the recent researches in organic chemistry. The author criticises the theory that enzymes are not a substance but a property, and adduces all the evidence for the theory of the chemical nature of the action of enzymes.

The question of the individuality of enzymes the author answers in the affirmative.

The mode of preparation of the different individual enzymes, and the favorable and unfavorable condition for their action is discussed in considerable detail, and sufficient room is given to the theoretical explanation of the experimental and practical findings. It seems, however, that the reversibility of the action of ferments is omitted in all the theoretical considerations of the author, and yet they could explain a good many facts for the explanation of which the author resorts to much more complicated views.

The chapters on industrial application of the enzymes read as interestingly as the theoretical discussions, and the book will undoubtedly be an inspiration to a good many workers in the line of biological chemistry.

The fact that the author verified most of the experimantal data of other investigators mentioned in the book makes the book all the more valuable.

Mr. Prescott deserves much credit for the good translation of the book.

P. A. LEVENE.

REPRINTS OF SCIENCE CLASSICS NO. 1. THE ANALYSIS OF AIR AND WATER, being selections from LAVOISIER'S ELEMENTARY TREATISE OF CHEMISTRY. Translated and annotated by C. E. LINEBARGER. 1902. Ravenswood, Chicago, Ill. The School Science Press. Double number, pp. 31. Price, 10 cents.

The purpose of the little pamphlet before us is to place in the hands of pupils of high schools and colleges the exceedingly beautiful and clear account which Lavoisier gives of those experiments which first laid a secure foundation for our present knowledge of air and water. Dr. Linebarger's idea is a most happy one. It is difficult to think of anything better than this little booklet for riveting the attention and awakening the interest of beginners in scientific study. It is well worthy of perusal by older chemists

as well, for we all have much to learn from the great master of our science. W. A. N.

STUDIEN ZUR KENTNISS DER ABHÄNGIGKEIT DER VISCOSITÄT DER FLÜSSIGEN KÖRPER VON DER TEMPERATURE UND VON IHRER CHEMISCHEN CONSTITUTION. By Alexius Batschinski. 101 pp. 17 × 25 cm. Moscow. 1901.

Though large enough to be a monograph, this is really a reprint of a journal article. The author has previously called attention to the fact that with most liquids the product of the internal friction into the absolute temperature is a constant. Data are given showing the application of this law to one hundred and forty-four different substances. In general, the agreement is good ; but anhydrides, acids, alcohols and water form exceptions. These are all substances which we consider as polymerized in the liquid state. WILDER D. BANCROFT.

THE EXPERIMENTAL STUDY OF GASES. By MORRIS W. TRAVERS, D.Sc. New York : The Macmillan Co.

Dr. Travers' book confines itself to methods of experiment which have been useful in researches on the properties of gases and to a description of some of the more important of such researches. It does not contain lecture experiments, nor instruction for beginners. In the selection of topics, it is well balanced, and as complete as can fairly be demanded of its 320 pages ; chapters on mercury pumps, on stop-cocks and other connections, on the collection and storage of gases, on reading instruments, and on calibration, have their due place. The chapters on the preparation of pure gases, on gas analysis, and on the determination of densities, are interesting and satisfactory, as are those on the relation of temperature, pressure, and volume, on vapor pressure and critical constants, and on specific heat.

The most interesting chapters, naturally, are those which have more or less to do with the newly discovered gases. That entitled "The Gases of the Helium Group" describes the method used in isolating argon, and that afterwards used to obtain it in considerable quantity, and narrates the steps which led to the discovery of helium, neon, krypton, and xenon. A chapter on the liquefaction of gases explains all the new principles which have been utilized and the new processes which have been used in liquefying gases since the time of the experiments of Pictet and of Cailletet. Here is found a clear account of Hampson's machine for liquefying air ; it is stated that this machine will

begin to deliver liquid air in four minutes from the time of starting it. A method is fully described by which liquid hydrogen may be obtained without great difficulty. A chapter entitled "The Manipulation of Liquefied Gases" will be thought by many to be the most interesting in the book. It treats of the separation of gases in a mixture by fractional distillation. One such separation was that by which, from a hundred liters of atmospheric nitrogen, there was obtained a residue containing ten per cent. of neon and helium; in the air, there is but one or two parts of neon in a hundred thousand, and perhaps a tenth as much helium. Another such separation is that of fifteen liters of argon; diagrams make clear the course of the experiment, by which, after two final distillations at the temperature of liquid hydrogen, neon was obtained in quantity sufficient for the determination of its density. A third such fractional distillation was that applied to liquid air, by which krypton and xenon were obtained; the course of this experiment is also made clear by the aid of diagrams. A proper end of this subject is made by the chapter on spectrum analysis, which contains convenient tables, as well as a map, of the spectra of the new gases.

The reading of proofs was careful; no misprints have been noted more serious than Hildebrand twice for Hillebrand, and Gimmingham for Gimingham. . Errors of fact are few and unimportant. Names of journals not published in England are cited somewhat carelessly; the Smithsonian Contributions to Knowledge appear as Proceedings of the Smithsonian Association, and the Annales de Chimie et de Physique is referred to in five different ways.

Dr. Travers' connection with the first workers on the new gases was so intimate, and his own part in some of the work was such, that he is especially well fitted to write this volume, which is a very welcome addition to scientific literature.

EDWARD W. MORLEY.

THE MANUFACTURE OF PAINT. By J. CRUICKSHANK SMITH. London: Scott, Greenwood & Co. 1901. 200 pp. Price, $3.00 net.

This author seems to know very well the kinds of machinery in use in England for making the cheaper grades of paint, and the illustrations are intelligently chosen and well executed. It is difficult for an American paint manufacturer to believe that modern high-class paint machinery has not yet found its way

into English factories, but very likely it is true. The only American machine described is one of the earlier forms of water-cooled mills; and the practical, technical points which one would like to find in a book of this sort, such as the values of different styles of dressing millstones for various kinds of work, the points of excellence to be aimed at in making particular paints, the nature and effect of the vehicles used, and the like,—such things as these are very scantily touched upon. It seems remarkable that no mention is made of the practice of mixing oil with wet white lead without preliminary drying, a practice of great commercial importance. In general, the information conveyed to the reader seems to be of the sort obtainable from the makers of paint machinery, rather than from experts in paint manufacture; accurate and useful as far it goes, but lacking in real knowledge of the subject. The book is one which should be of interest and use to the beginner but is not complete enough to serve the advanced manufacturer. A. H. SABIN.

LEÇONS SUR LA THEORIE DES GAZ. L. BOLTZMANN; traduites par A. GALLOTTI. Paris: Gauthier-Villers. 1902. Price, 8 francs.

Boltzmann is one of the three great mathematicians to whom the development of the kinetic theory of gases is mainly due. The present volume contains a translation of the first half of his lectures, originally published in 1896 and 1898, and gives a systematic account of the mathematical results attained by the joint labors of Maxwell, Clausius and Boltzmann.

Professor Gallotti's translation is clear and accurate; some sentences are even more perspicuous than in the original. Professor Brillouin has furnished an historical introduction and some comments on certain steps in the mathematical discussions of the author. EDWARD W. MORLEY.

THE MANUFACTURE OF MINERAL AND LAKE PIGMENTS. BY DR. JOSEF BERSCH. TRANSLATED BY A. C. WRIGHT. London: Scott, Greenwood & Co. 1901. 476 pp. Price, $5.00 net.

This admirable book was evidently written by a thorough chemist who is also a practical color-maker. Not many technical points escape mention and the book is valuable not only for reference but for daily use. The chapters on "Black Pigments," "Vermilion," and "Ultramarine," are especially valuable, as presenting an intelligible account of processes on which very little practical information is available.

It is, of course, impossible to write a book which nobody can find fault with; for example, our author gives barium chromate as a pigment under the name of "Permanent Yellow," and omits any mention of strontium chromate; the former is a very inferior color, not known in this country, while the latter, known under the same name and also as "Perfect Yellow," is one of the most beautiful pigments known and, in spite of its low opacity, is considerably used. Also in the chapters devoted to "Metallic Pigments" and "Bronze Pigments," no mention is made of metallic aluminum, one of the most valuable and widely used pigments in this class.

The part of the book devoted to "Lakes" is, in the judgment of the reviewer, hardly up to the standard of the rest of the book, not because of what it contains but what it leaves out. The author seems to have felt less interest in this subject and has treated it less in detail, but it seems to be correct as far as it goes. The book, as a whole, is very satisfactory.

A. H. SABIN.

THE ELEMENTS OF PHYSICAL CHEMISTRY. Second Edition. By J. Livingston R. Morgan. New York: John Wiley and Sons. 1902. 13 x 19 cm. x + 352 pp. Cloth. Price, $2.00.

This book does not differ essentially from the first edition, which appeared in 1898, so that it would be superfluous to give an outline of its contents. The author states that he has endeavored, (1) to bring the subject matter up to date, (2) to make, wherever possible, the relations clearer than before, and (3) to make the book more useful to those studying the subject without an instructor. The changes made consist of a number of minor omissions and additions; a transposition of the chapter on the rôle of the ions in analytical chemistry, so as to form a part of the chapter on chemical change; and the addition of a final chapter containing problems for drill work.

The author has exerted himself to correct the numerous mistakes contained in the first edition; and yet, the new edition is by no means free from errors. It is impossible to cite all of these in detail here, but a few must be given by way of illustration. Thus on page 70 is the statement, "The surface-tension x of a liquid is the force in grams, dynes (or milligrams) which is necessary to form a surface one centimeter (millimeter) in length." The theory ascribed to Brühl on page 268 is simply the Nernst-

Thomson view of the relation between the dielectric constant of a solvent and its so-called dissociating power. The new idea that Brühl does put forth in the article cited, is that dissociating power is due to the unsaturated condition (*i. e.*, to spare valences) of solvents. On page 269 we read, "Because substances dissolve and go into the ionic state with a loss of heat energy, does not show that there is a loss of energy to the system, but only that by the transformation heat energy as well as electrical energy are given up."

The italicised statement on page 93 that "the osmotic pressure depends upon the solute and is independent of the nature of the solvent," and that on page 100, "those substances, and only those, which give abnormal osmotic pressures in solution are capable of conducting the electric current, and if they are dissolved in other solvents in which they behave normally, they lose this power", can no longer be considered "up to date."

A brief treatise on general physical chemistry which devotes such an undue proportion of its space to the exposition of the theory of electrolytic dissociation and its applications (without even attempting to indicate the shortcomings of this hypothesis) as this book does, can at the present stage of the development of the science, hardly claim to present the subject in a fair, well-balanced form. LOUIS KAHLENBERG.

OUTLINES OF ELECTROCHEMISTRY. BY HARRY C. JONES. New York: The Electrical Review Publishing Co. D. Van Nostrand Company. 1901. vi + 106 pp. Price, $1.50.

Contributed originally to the pages of the *Electrical Review*, the articles forming the chapters of this book are designed for the information of those interested in or concerned with electrical engineering, as well as for the student of the subject from the purely scientific standpoint. The author disclaims any pretensions to their forming a systematic treatise, yet the subject is treated in such a manner as to introduce the reader by comparatively easy steps to a knowledge of osmotic pressure and the ionization theory of solution, and of the bearings of these matters upon electrochemistry. The later chapters deal particularly with the calculation of the electromotive force of galvanic elements. While it may be admitted that, upon the whole, the book conveys to the so-far initiated reader a clear idea of the subject, and that a number of the chapters leave little to be desired as semi-

popular articles, there are parts which can scarcely be regarded as quite satisfactory. On page 40, for instance, under the heading of "The Present Theory of Electrolysis," sufficient evidence is not furnished to carry conviction regarding the assertion that "we must abandon the theory of electrolysis which involves the secondary decomposition of water." When there are two different kinds of anions around the anode in electrolysis—in the case of hydrochloric acid, for example, chlorine ions from the ionized acid and hydroxyl ions from the ionized water—is it quite obvious, as the author asserts, that the ions which will give up their charges to the anode are the ones which hold them less firmly? Has the effect of the varying proportions in which the two kinds of ions may be present not been overlooked here? The author's statements seem convincing enough where only exceedingly low current densities are in question; but is it justifiable to make the unqualified assertion that "the anions move to the anode, but do not give up their charges; the hydroxyl anions from the water give up their charges instead?" (page 42). How is the formation of persulphuric acid at the anode to be explained on such an assumption? It is true that a few pages further on the effect of increased current density is referred to, but in such a way that the uninformed reader is very likely to overlook its importance.

A rather misleading description of the porous earthenware vessel used as a support for the semipermeable membranes employed in making osmotic pressure determinations, is given on pages 6 and 7, where it is referred to as "porcelain," whereas true porcelain is really non-porous.

The rather inconvenient shape of the book is, no doubt, due to the type having been set up originally in column form for the review in which the articles appeared. The matter should have undergone more careful revision before being issued in book form, as a number of mistakes have escaped correction. Vagaries of linotype setting are obviously responsible for the omissions and dislocations, on page 63, column 2, lines 5 and 6, and on page 83, column 2, line ten from foot. Humphrey Davy and Borschers appear instead of Humphry Davy and Borchers respectively (pages 2, 32, 43). A figure should have been prepared for page 83, to conform with the description in the text. It can scarcely be doubted that Walker would object to being represented as the author of the general electrolytic method, mentioned on page 45,

of passing from one dibasic acid to another richer in carbon atoms.

In conclusion, the following pronouncement of the author may be warmly commended: "In a word, the proper place to lay the foundation for the career of the practical man is in the University." LEONARD DOBBIN.

DRYING OILS, BOILED OIL, AND SOLID AND LIQUID DRYERS. By LOUIS EDGAR ANDÉS. London: Scott, Greenwood & Co. 1901. 342 pp. Price, $5.00 net.

In times past this author has been a serious offender in the way of writing books which were merely compilations of what other people had said or guessed, so that we look with suspicion on a new book from him; but in this instance we are agreeably disappointed. Mr. Andés evidently knows something about drying oils, and has a lot of practical experience in their treatment and use. It is the best book on the subject and is pretty well up to date. The book indeed contains many of the old, useless, and impracticable formulae, familiar to all students of the subject, but these are compensated by remarks from the author's own experience which are fairly luminous with good sense and accurate knowledge, such as characterize the chapter on "Dryers." To get the real value of the book one must differentiate between the things which the author knows and those which he has merely read about; but to one reasonably familiar with the subject, this is not difficult, and to such the book will be found very useful. It is worth buying. A. H. SABIN.